THE JOURNAL

OF THE

AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. L FEBRUARY 1955 No. 2

CONTENTS:

Candidates for the 1955 Election - - - - - - - 64

The Chemistry of Vegetable Tannins XII, Chestnut
By R. C. PUTNAM and W. R. BROWNE - - - - - 64

The Preparation and Tanning Properties of Phenolic Derivatives of Lignosulfonic Acid: Part I
By W. R. KENZIE and A. M. WILSON - - - - - 85

The Preparation and Tanning Properties of Phenolic Derivatives of Lignosulfonic Acid: Part II Application of the Cresol Derivative to the Retanning of Chrome Leather *By* H. B. MARSHALL and M. KRIZSAN 96

Abstracts - - - - - - - - - - - - - 107

SUBSCRIPTION: Members $12.00 a Year Non-Members $15.00

Published Monthly by

THE AMERICAN LEATHER CHEMISTS ASSOCIATION

PUBLICATION OFFICE, EASTON, PA.

Entered as Second-Class Matter at Post Office, Easton, Pa.
Acceptance for Mailing at Special Rate of Postage as Provided for in Section 1103.
Act of October 3, 1917, Authorized July 16, 1918

COPYRIGHT, 1955, THE AMERICAN LEATHER CHEMISTS ASSOCIATION

Reliable Direct Sources the World Over

FOR

VEGETABLE TANNING MATERIALS

QUEBRACHO
WATTLE EXTRACT
WATTLE BARK
MANGROVE BARK
MYRABOLAMS & EXTRACT
VALONEA & EXTRACT
DIVI DIVI
CUTCH
SUMAC—LEAF & GROUND
TARA—PODS & POWDER
OAKWOOD EXTRACT, Swedish
LARCHBARK EXTRACT, Swedish

▼

U. S. of A. Sales Agents for "N.C.S." Brand South African Wattle Extract

U. S. of A. Sales Agents for "SENS" Brand Powdered Valonea Extract

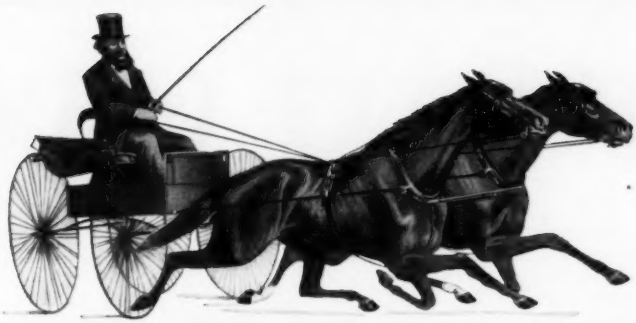
The Olson Sales Agency

Import · Export

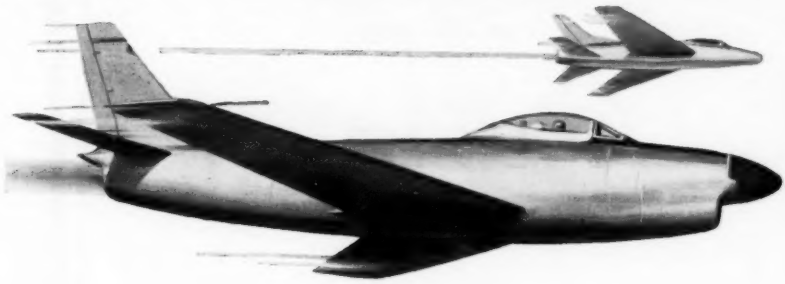
369 Lexington Avenue, New York 17, N. Y.

Cable Address:
"COROSAGE"

Telephones:
LExington 2-3733
2-3734
2-3735



1866...FROM HORSE AGE TO JET AGE...1955



89 Years of continuous improvement *have made Gargoyle*

the most trusted name in leather oils and greases!

It started in 1866 with the first harness oil. And today, the Gargoyle tradition for making fine leather oils and greases has carried right over into the jet age.

The Sulfolines, the Curriers Greases, the Solenes and Waterproofing Compounds—all have kept pace with scientific progress in the tanning industry.

These Gargoyle products are just a small part of our complete line of leather oils, greases and specialties—all made under the most exacting standards to assure top quality.

Take advantage of our products, services and technical facilities to improve *your* operation!

SOCONY-VACUUM

GARGOYLE

LEATHER OILS AND GREASES

SOCONY-VACUUM OIL COMPANY, INC., TANNERS DIVISION, 26 BROADWAY, NEW YORK 4, N. Y.

SPRUCE EXTRACT

POWDERED SUPER SPRUCE

LACTANX

■

Robeson Process Company

General Offices: 500 Fifth Avenue, New York, N. Y.

Operating Plant at Erie, Pa.

MECO EXTRACT

ONE GRADE—THE BEST

CHESTNUT WOOD EXTRACT

All Concentrations, Liquid to Dry Powder

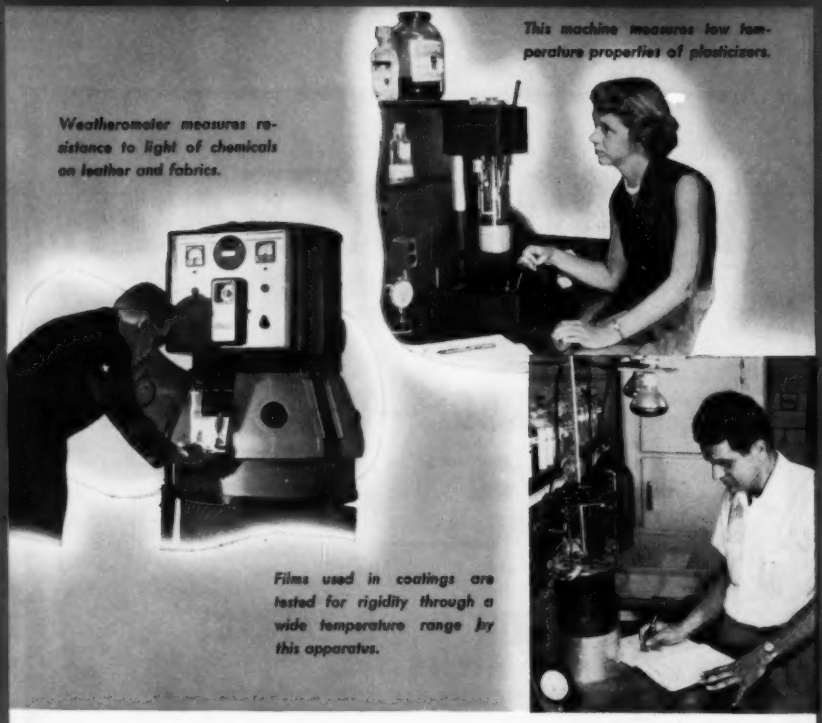
Teas Extract Co.

6400 Centennial Boulevard

NASHVILLE 9, TENNESSEE

TENNESSEE PLANT
Nashville, Tenn.

ANDREWS PLANT
Andrews, N. C



This machine measures low temperature properties of plasticizers.

Weatherometer measures resistance to light of chemicals on leather and fabrics.

Films used in coatings are tested for rigidity through a wide temperature range by this apparatus.

THE SEARCH THAT NEVER ENDS

Once in awhile the question is asked: "What has been the effect on Rohm & Haas leather chemicals of the spread of the company's interest into other fields?" The answer is simple: Chemicals which might not otherwise have been made are now available to the tanner. This has resulted in the development of products of highest quality whose range of usefulness to the tanner is steadily being extended.

Important as our leather business is, it could not by itself support the fundamental research in various fields which has resulted in the development of new and improved leather chemicals for the tanner.

A case in point is ZIRCOTAN, the zirconium tanning agent for producing through-white leather. Initially our interest in zirconium compounds centered around their use as opacifiers for porcelain enamel. Subsequent work on the chemistry of zirconium led to the development of ZIRCOTAN.

Another example is our PRIMAL acrylic leather finishes. This company is the pioneer in acrylics. Knowledge of the toughness and permanent flexibility of acrylic polymers made possible the development of PRIMAL emulsions.

CHEMICALS FOR INDUSTRY

ROHM & HAAS COMPANY

WASHINGTON SQUARE, PHILADELPHIA 5, PA.

Representatives in principal foreign countries

ZIRCOTAN *and* PRIMAL *are trademarks, Reg. U.S. Pat. Off. and in principal foreign countries.*

ARKO FAT LIQUORS

FORMULATED FOR PERFECT TAKE-UP AND NOURISHMENT

ARKO FAT LIQUOR L M:—Especially made for horsehide, cow sides glove and garment leather. Excellent for goatskin glove and garment.

ARKO FAT LIQUOR L C:—A superior oil for deer, pig, cape and cabretta glove leather.

ARKO FAT LIQUOR C B:—Processed sulfonated cod oil for vegetable leathers.

ARKO FAT LIQUOR D:—For very fine suede leathers where dryness, nourishment and stretch are required.

Information, samples and demonstration upon request.

ARKANSAS COMPANY, Inc.
Newark, N. J.

Manufacturers of Industrial Chemicals for over 50 years

MEAD CHESTNUT EXTRACT

is a superior tanning material, made by America's largest producer of vegetable tanning extracts

Repeated experience has shown:

A. Chestnut tanned leathers do not oxidize, darken on exposure to light, or develop an uneven color on aging, as do leathers tanned with many other materials, vegetable or synthetic.

B. Since the tanning system demands acid, the use of chestnut, with its plumping acidity, saves you money.

C. Mead Chestnut Extract eliminates up to 28% of leachhouse losses.

D. There are no hidden costs. When you use Mead Chestnut Extract, no time- and money-consuming preparation is required.

THE MEAD CORPORATION

Tannin Extract Division, Lynchburg, Virginia

JACQUES WOLF

Chemicals

PRODUCE HIGH GRADE

LEATHER

SYNEKTAN 0-230 **FAT LIQUOR L-90B**
SYNEKTAN 0-272 **FAT LIQUOR 0-270**

For White Leather At Reasonable Cost
White Leather In Sheep, Goat, Calf Or Sides
White Tan In Combination With Chrome
White Nubuck, White Suede
White Bleached Chrome Stock
White Extract Type Of Leather

FUNGIZYME BATES
AS — BS — CS

Pancreatic bating salts of standard, controlled quality.

SULPHONATED OILS (Various Bases)

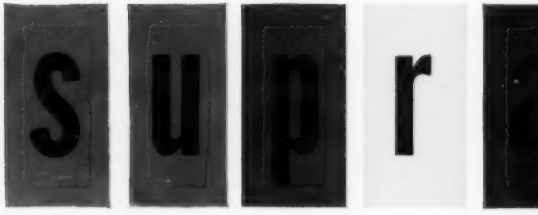
MONOPOLE OIL (For Finishing)

SAMPLES AND INFORMATION UPON REQUEST.

JACQUES WOLF & CO.
Chemicals PASSAIC, N. J.

Branches:
Carlstadt, N. J.
Los Angeles, Calif.

. . . to enhar
the natur
of leath



Because of their high surface
properties, the Supranols are
all types of leather—whenev
shade and fastness to crockin

supranols:

- enhance—rather than conce
- work equally well with all t
- provide good fastness to li
- impart excellent uniformity
- give a transparent, high su
- dye level—glaze true to sh

Our technical department an
your service. For samples of t
on a specific problem—write

From Reseat

gdc gaf

GENERAL DY
A SALES DIVISION OF GEN
435 HUDSON STREE

BOSTON • CHARLOTTE • CHATTANOOGA • CHICAGO • LOS ANGELES • NEW

nance
tural beauty
athers

anols®

surface color value and level dyeing
nols are of special interest for coloring
whenever brilliance, uniformity of
crocking are of major importance.

an conceal—the natural grain
vith all types of tannages
ess to light, washing and crocking
formity of shade
high surface color value
ue to shade

ment and research facilities are at
ples of the Supranols—or for assistance
—write or call our nearest office.

Research to Reality

DYESTUFF COMPANY
F GENERAL ANILINE & FILM CORPORATION
TREET • NEW YORK 14, NEW YORK

SELES • NEW YORK • PHILADELPHIA • PORTLAND, ORE. • PROVIDENCE • SAN FRANCISCO

1st CHOICE

for Higher Quality Leather Production

L.H. LINCOLN & SON, INC. LINCO PRODUCTS COUDERSPORT, PA.

Better Grading Figures!
Better Cutting Figures!
Overall Economy!

Extracts — Pancreatic Bates — Fillers
Sole Leather Finishes - Tanners Sugar
Tanners Lime — Chemicals

L.H. LINCOLN & SON, INC.
COUDERSPORT, PA.

PENETRATION

scores increased sales!

Your customers will welcome the improved performance value of penetrated side and kid leathers that eliminate the need for edge staining by the manufacturers—your customers. Their savings in time and labor can mean increased business for you.

Geigy technicians will be glad to recommend dyestuffs for producing full shades that achieve the desired penetration while maintaining tinctorial surface strength. Formulations will be custom-engineered, consistent with your particular tannages and processing requirements.

Call or write Geigy without delay.

GEIGY DYESTUFFS
DIVISION OF GEIGY CHEMICAL CORPORATION
89-91 BARCLAY STREET, NEW YORK 8, NEW YORK

Geigy

dyestuff makers since 1859

BRANCH OFFICES: BOSTON • CHARLOTTE, N. C. • CHICAGO • LOS ANGELES PHILADELPHIA
PORTLAND, ORE. • PROVIDENCE • TORONTO • IN GREAT BRITAIN: The Geigy Co., Ltd., Manchester

QUEBRACHO EXTRACTS

"SUPREMO"
BRAND
SOLID-ORDINARY

"LUNA"
BRAND
COLD WATER SOLUBLE

INTERNATIONAL PRODUCTS CORPORATION

29 BROADWAY, NEW YORK 6, N. Y.

The Only American Manufacturer of Quebracho In South America

FACTORY AT PUERTO PINASCO, PARAGUAY

MANUFACTURERS:
LIQUID
QUEBRACHO
EXTRACTS
•
FACTORY:
Staten Island, N. Y.

IMPORTERS:
MYRABOLAMS
WATTLE BARK
DIVI-DIVI
VALONIA
ETC.

Representatives:

Harvey J. Boutin & Son
San Francisco, Calif.

Yocum Faust, Limited
London, Canada

Gonzalez, Ramirez y Cia
Havana, Cuba

The R. J. Vogel Company
Mexico City, Mexico

Buffing white leather at S. B. Foot Tanning Company, Red Wing, Minnesota

How TANAK® MRX gives you thicker grain . . . for better white leather buffing

While normal syntan bleaches give good white color, they tend to produce poor break, plus soft and loose bellies and flanks. Now, however, you can get plumper grain, with *improvements* in break, temper and strength by using TANAK MRX in your tanning or retan solutions.

For chrome whites, this permits deeper buffing to remove grain defects without sacrificing normal grain thickness. It also enables you to upgrade your colored and natural back stocks—a clear chance for a better competitive position in your markets.

TANAK MRX is a development of Cyanamid's Technical Staff, working closely with tanners to improve leather through chemistry. Cyanamid offers chemicals for virtually every tanning process, plus the facilities of a modern application laboratory where new products and processes can be thoroughly explored.

To make better leather through chemistry...

The phenol-base SUPRAK® syntans are showing the way to better, softer leathers—giving mordant action, leveling dyes and helping to build fullness.

AMERICAN Cyanamid COMPANY

LEATHER CHEMICALS DEPARTMENT

30 Rockefeller Plaza, New York 20, N. Y.

In Canada: North American Cyanamid Limited, Toronto and Montreal

To prevent SPOILAGE

USE.. BSM-11 or BUTROL

as part of Good housekeeping practice

BSM-11 is highly effective in controlling the growth of microorganisms which digest hide substance during processing. BSM-11 is a liquid, thus easily added to the systems directly from the drums.

It has been demonstrated in many tanneries that the synergistic combination of bactericides and fungicides in BSM-11 provides efficient, economical control of bacteria, molds and yeasts which damage skins and hides.

Our representative will give technical assistance on the most effective use of BSM-11 in your process.

BUCKMAN LABORATORIES, INC.

Manufacturing Chemists • Memphis 8, Tennessee • Representatives in Most Countries

MICROORGANISM CONTROL SPECIALISTS

AT YOUR SERVICE . . .

Let our *67 years* of specialized experience work for you . . . profitably

ATLAS

Guaranteed **OILS**

- **NEATSFOOT OILS**
- **SULPHONATED COD OILS**
- **SULPHONATED NEATSFOOT OILS**
- **SPLIT OILS**
- **MOELLONS, and many specialty Products**

ATLAS REFINERY SINCE 1887 QUALITY LEATHER OILS NEWARK, N.J.

A Name and Symbol Pre-eminent in the Tannery Industry

● For over half a century, ATLAS has been a leader in the production of Quality Oils for the Tanning Industry, through extensive research to serve you better. ATLAS specialized research, plus many years of practical experience in the production of consistently high-quality, guaranteed oils is your assurance of uniformity to meet definite specifications. Give your leathers the "quality look" with ATLAS Oils.

ATLAS *Refinery, Inc.*

142 LOCKWOOD ST. NEWARK 5, N. J.

MICROORGANISM CONTROL SPECIALISTS

THE RIVER PLATE CORPORATION

EXTRACTS & RAW TANNING MATERIALS

QUEBRACHO

solid:
CF del C CROWN REALTAN

liquid:
SM . . . SMS

ground or spray dried
ORDINARY . . . PUREX

WATTLE

solid:
KENMOSA ELEPHANT

liquid:
WATEX

ground or spray dried
WATTLE

MYRABOLAM

spray powdered & solid

CHESTNUT

spray powdered & solid

MANGROVE & WATTLE BARK
WHOLE & CRUSHED MYRABOLAMS
VALONEA TARA SUMAC DIVI DIVI
SPRAY POWDERED MANGROVE & VALONEA

Importers and Processors

THE RIVER PLATE CORPORATION
CHRYSLER BLDG., NEW YORK 17, N. Y. *Plant:* NEWARK, N. J.

Subsidiary: THE TANNIN CORPORATION of MASS. Office & Plant: Peabody, Mass.

WATTLE

IS THE RIGHT EXTRACT FOR UPHOLSTERY LEATHER

SOME of the finest upholstery and bag leathers made in the world today are tanned in liquors containing up to 70% or more of Wattle Bark Extract.

By careful blending of this unique extract with other tannins, especially pyrogallol materials such as Myrabolams, a balanced blend is produced that is speedy and yet gives all the characteristics to the finished product usually associated with leather formerly produced by the old bark tannages.

If you are interested in the production of upholstery, bag case or dressing leather of any kind, try Wattle in your liquors and see the improvement in the resulting leather.

WATTLE MAKES GOOD LEATHER

SOUTH AFRICAN WATTLE EXTRACT MFRS. ASSO.
Pietermaritzburg, Natal, Union of South Africa
KENYA WATTLE MANUFACTURERS ASSOCIATION
Nairobi, Kenya, East Africa

are you worried? about your supply of:

chestnut

you should know that

60 up - to - date factories

located in the woodlands of France, Italy and Switzerland can meet your needs thanks to their yearly production of over 2 000 000 bags of pure chestnut extracts

If you wish

for your sole leather: Maximum degree of tannin fixation
Highest yield
Better firmness and waterproofness

for your chrome retan uppers, welting, upholstery leathers: Excellent tensile and stitching strength together with good suppleness and colour.

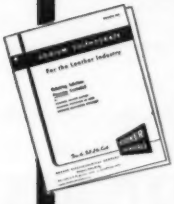
use the Astringent and Adjusted CHESTNUT EXTRACTS from the living trees of Western Europe

What Hooker Sodium Sulfhydrate does for the Leather you make...

SOLE LEATHER—With Hooker Sodium Sulfhydrate, you can increase sulfide strength of the unhairing solution just as desired, and still keep alkalinity low. This means easy unhairing in limited time. Hides are ready when desired—without loss of hide substance from long immersion. *Results:* a minimum of swelling . . . greater yield of tight, solid, smooth-grained leather . . . a significant saving of time and extra operations in the beam-house.

CALFSKINS AND HORSEHIDES—The tender grain of these skins is protected by Hooker Sodium Sulfhydrate from excessive swelling and plumping caused by high alkalinity. With Sodium Sulfhydrate, a minimum of swelling takes place, resulting in a better yield of fine, smooth leather.

GOATSKINS—Destructive bacterial action is held to a minimum, because Hooker Sodium Sulfhydrate increases the solubility of the lime and permits more constant pH value than with Sodium Sulfide. Sulfide content can be built up, with low alkalinity. Alkalinity can be increased or held as desired, without affecting sulfidity. *Result:* Greatly simplified control of quality, even with skins that vary widely in sensitivity.



When dissolved in lime, Hooker Sodium Sulfhydrate forms only half as much caustic soda as the same quantity of Sodium Sulfide forms. This gives you precision control of unhairing solutions—and many other advantages. Write today for a copy of Hooker Bulletin 500, "Sodium Sulfhydrate for the Leather Industry," which suggests unhairing procedures for various leathers.

HOOKER ELECTROCHEMICAL COMPANY

3 UNION ST., NIAGARA FALLS, N. Y.
CHICAGO, ILL. - NEW YORK, N. Y.
LOS ANGELES, CALIF. - TACOMA, WASH.

HOOKER CHEMICALS ®

CHLORINE • SODIUM TETRASULFIDE • SODIUM SULFIDE
CAUSTIC SODA • MURIATIC ACID • PARADICHLOROBENZENE

10-1398

BARKEY

Importing Co. Inc.

44 EAST 53rd STREET • NEW YORK 22, N. Y.

IMPORTERS

VEGETABLE TANNING EXTRACTS AND RAW MATERIALS

- Wattle Bark
- Wattle Extract
- Quebracho Extract
- Mangrove Bark
- Valonia Cups, Beards
- Divi divi
- Valonia Extract, Valex Brand
- Sicily Sumac
- Myrabolans

SOLE AGENTS FOR UNITED STATES & CANADA

for

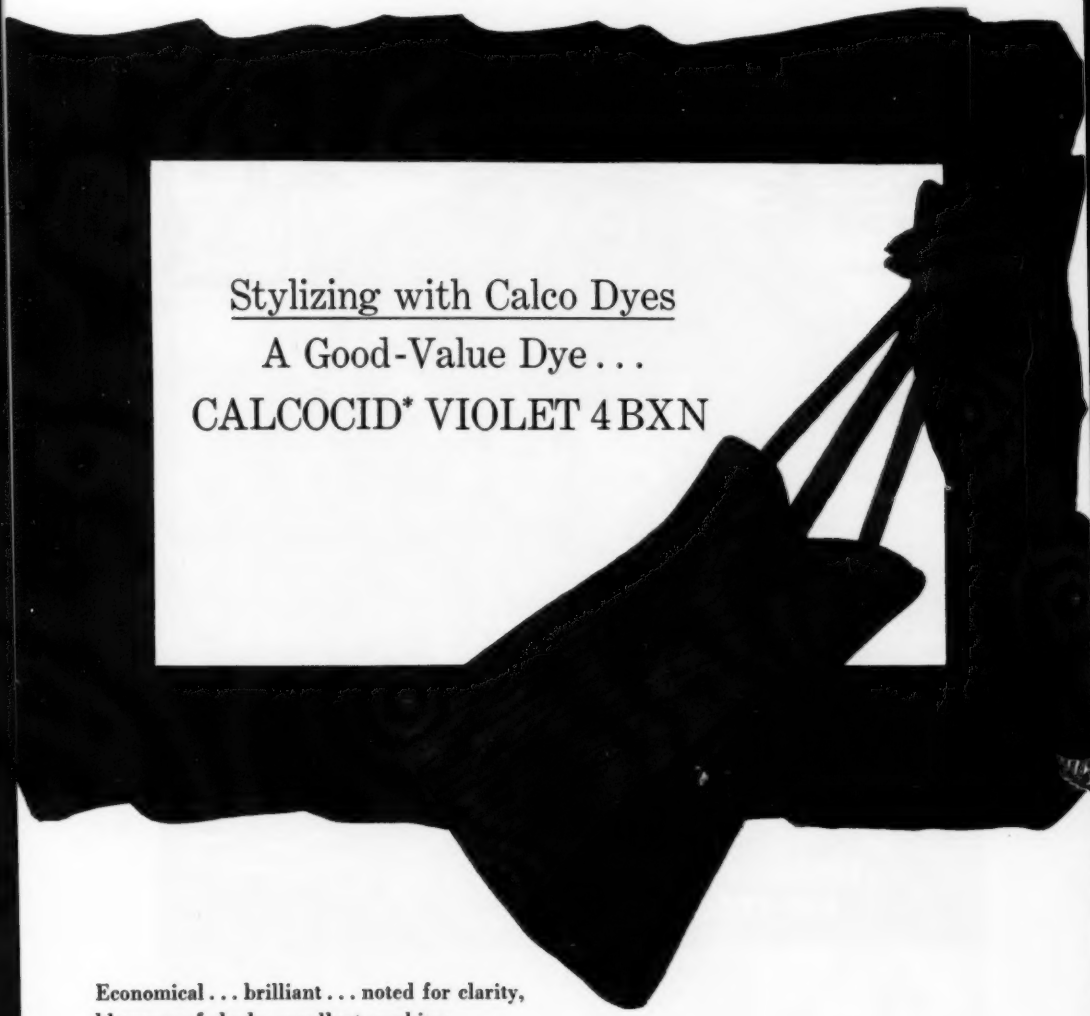
ITALIAN CHESTNUT EXTRACTS

SOLID & POWDERED

Produced by

LEDOGA S. p. A.

MILANO, ITALY



Stylizing with Calco Dyes

A Good-Value Dye . . .

CALCOCID* VIOLET 4BXN

Economical . . . brilliant . . . noted for clarity, blueness of shade, excellent working properties at heavy percentages — that's Calcocid Violet 4BXN.

Recommended for finishing as well as drum coloring, this dye is used extensively for coloring garment, lining, upholstery, bag and dressed side leathers. Calcocid Violet 4BXN is popular for imparting rich tones to black and brown suede and grain leathers.

Your Cyanamid Dyestuff representative will gladly give you full information on this and other dyes in the extensive Cyanamid line.

*Trade-mark

NORTH AMERICAN CYANAMID LIMITED
DYESTUFF DEPARTMENT
MONTREAL AND TORONTO

Calco®

AMERICAN Cyanamid COMPANY

DYESTUFF DEPARTMENT
BOUND BROOK, NEW JERSEY

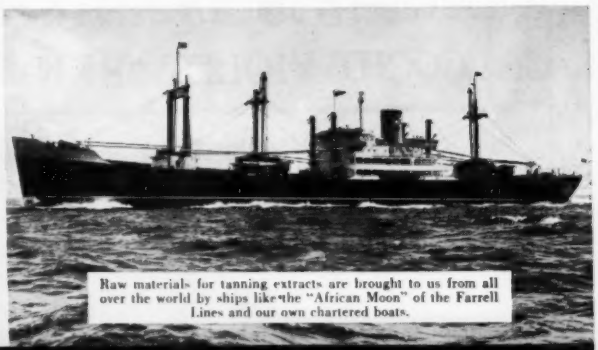
NEW YORK • CHICAGO • BOSTON • PHILADELPHIA • CHARLOTTE • PROVIDENCE
LOS ANGELES • PORTLAND, OREGON

WATTLE BARK — *from Africa*

SUMAC — *from Sicily*

DIVI-DIVI — *from Santo Domingo*

GAMBIER
— *from Malayan Straits*



Raw materials for tanning extracts are brought to us from all over the world by ships like the "African Moon" of the Farrell Lines and our own chartered boats.

MYRABOLAM — *from India*

The J. S. Young Company

ONE OF AMERICA'S FOREMOST IMPORTERS AND PROCESSORS OF *Tanning Extracts*

QUERBRACHO
— *from the Argentine*

CHESTNUT WOOD *Extract*
— *from France and Italy*

For nearly a century — since 1869 — The J. S. YOUNG CO. continuously has imported, processed and manufactured — in its modern 8½-acre Baltimore plant — highest quality tanning extracts for the industry.

They include:

LOGWOOD • WATTLE BARK • SUMAC • DIVI-DIVI • GAMBIER • QUERBRACHO • MYRABOLAM
OSAGE ORANGE • CHESTNUT WOOD EXTRACT • FUSTIC • HYPERNIC • TANNIC ACID

We are also manufacturers of the famous CHEMBARK natural tanning extracts for the Chemtan Co. and other special products.

The J. S. YOUNG CO.

2701-2733 Boston St., Baltimore 24, Maryland

Experienced technical advice available on request from Baltimore or from any of our branches.

Branches: **PHILADELPHIA • MILWAUKEE • PATERSON, N. J. • DANVERS, MASS.**

DEVELOPMENT AND

INTRODUCTION OF

BETTER **CHEM**ICALS FOR **TAN**NING

Accurate weighings in less than thirty seconds . . . . . .

METTLER BALANCES including SEMIMICRO and MICRO

- ▶ RAPID WEIGHING—by dialing built-in weights
- ▶ CONSTANT SENSITIVITY
- ▶ DIRECT READING
- ▶ SINGLE PAN
- ▶ SAPPHIRE KNIFE EDGES AND PLANES

1888-C.

ANALYTICAL BALANCES, Mettler. Single pan, direct reading, rapid weighing, accurate Balances with built-in Stainless steel weights operated by dials on front panel. Made in Switzerland and in satisfactory use throughout the world for the past eight years; now assembled—with the exception of the Micro model—and serviced in maker's U.S.A. branch.

Operate on the principle of weighing by substitution on a single pan with beam subject to constant load throughout the entire range, which method is recognized as highly accurate. Operation is simple and weighings can be completed in less than 30 seconds. Total weight is read directly from indicator on front panel. Sensitivity is constant throughout the weighing range.

The specially engineered packing includes all tools necessary for installation.

1867-J. Balance, Analytical, Mettler B-5, capacity 200 grams, accuracy ± 0.1 mg. With air damper and transformer for 110, 125, 145 or 220 volts, 50 or 60 cycles a.c., but without magnifier-light shield. **895.00**

1888-C. Balance, Semimicro, Mettler B-6, similar to 1867-J but with capacity 100 grams, accuracy within optical range ± 0.02 mg, accuracy of entire set of weights ± 0.1 mg, and with magnifier-light shield. **995.00**

1888-M. Balance, Microchemical, Mettler M-5, capacity 20 grams, accuracy within optical range ± 0.002 mg, accuracy of entire set of weights ± 0.02 mg. With front radiation shield and magnifier-light shield. **1,150.00**

More detailed information sent upon request.

QUALITY AND SERVICE
A.H.T.CO.
PHILA. U.S.A.
LABORATORY APPARATUS

ARTHUR H. THOMAS COMPANY

Laboratory Apparatus and Reagents

WEST WASHINGTON SQUARE PHILADELPHIA 5, PA.

Teletype Services: Western Union WUX and Bell System PH-72

JOURNAL OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. L FEBRUARY 1955 No. 2

DEAN WILLIAMS ..... *Editor*

EDITORIAL BOARD

H. B. MERRILL, R. E. PORTER, R. B. HOBBS, J. H. HIGHBERGER, F. O'FLAHERTY, H. G. TURLEY

Only such correspondence as pertains to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Correspondence in reference to subscriptions, advertising and other business should be addressed to the Secretary, Dept. of Leather Research, University of Cincinnati, Cincinnati 21, Ohio.

Checks for subscriptions and advertisements should be made payable to the American Leather Chemists Association.

Subscriptions—Members, $12.00 annually; Non-members, $15.00 annually.

Published monthly by the American Leather Chemists Association.

Entered as Second-class Matter at the Post Office at Easton, Pa.

Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917, authorized July 16, 1918.

Copyright 1955, by the American Leather Chemists Association.

PAST PRESIDENTS OF THE A. L. C. A.

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, F. P. VETCH, W. K. ALSOP, L. E. LEVI, C. R. OBERFELL, R. W. GRIFFITH, C. C. SMOOT, III, J. S. ROGERS, LLOYD BALDERSTON, J. A. WILSON, R. W. FREY, G. D. McLAUGHLIN, FRED O'FLAHERTY, A. C. ORTHMANN, H. B. MERRILL, V. J. MLEJNEK, J. H. HIGHBERGER, DEAN WILLIAMS, T. F. OBERLANDER, A. H. WINHEIM, R. M. KOPPENHOEFER, H. G. TURLEY.

OFFICERS 1954-'55

President—E. S. Flinn, Ardslea, Route 8 Chillicothe, Ohio.

President-Elect—E. B. Thorstensen, S. B. Foot Tanning Company, Red Wing, Minnesota.

Secretary-Treasurer—Fred O'Flaherty, Department of Leather Research, University of Cincinnati, Cincinnati, Ohio.

Council

R. G. Henrich, Surpass Leather Company, 9th and Westmoreland Streets, Philadelphia 40, Pennsylvania.

H. R. Wilson, B. D. Eisendrath, Memorial Laboratory, 702 Racine Street, Racine, Wisconsin.

J. R. Kanagy, 9922 Sutherland Road, Silver Spring 5, Maryland.

Mieth Maeser, United Shoe Machinery Corporation, Research Division, Balch Street, Beverly, Massachusetts.

Dominic Meo, Jr., Salem Oil and Grease Company, Salem, Massachusetts.

CANDIDATES FOR THE 1955 ELECTION

Candidates for Council:

MALCOLM H. BATTLES
ELL DEE COMPTON
ALFRED G. FLEISCH
HENRY B. MILLER
ROBERT STUBBINGS
PHILIP H. WAITE

The above slate of candidates has been prepared by the Nominating Committee.

JOHN W. HARNLY
J. HERBERT STUMPF
HENRY B. MERRILL, *Chairman*

Members Note:
Article V-2, Nominations (c)
Additional candidates may be nominated by petitions, signed by 15 or more active members. Such petitions shall reach the Secretary not later than April 1st, and shall contain a statement of the willingness of the nominee to serve if elected. No member shall sign more than one petition for each office to be filled.

The Chemistry of Vegetable Tannins XII, Chestnut

ROBERT C. PUTNAM* and WILLIAM R. BROWNE**

United Shoe Machinery Corporation
Research Division
Beverly, Massachusetts

In 1918 Perkin and Everest [1] classified vegetable tannins into three groups:
1. Depsides or gallotannins (contain ester groups)
2. Ellagitannins (contain ellagic acid groups)
3. Phlobatannins.

Freudenberg [2] then suggested a division into two main groups. The first included all hydrolysable tannins; the second, non-hydrolysable or phlobatannins.

A. GALLOTANNIN

Gallotannin is obtained principally from gallnuts, although it has been found in a great many plants. On treatment with dilute acid or alkali, it yields gallic acid. Early workers failed to give sufficient attention to purification and many reported constituents were later found to be impurities.

*Present address: United States Testing Company, Hoboken, New Jersey.
**Present address: Boston University, Boston, Mass.

Gallotannin was reported to contain verying quantities of glucose, analyses showing values from zero to more than twenty per cent. Fischer and others [3] found that its acid hydrolysis yielded one molecule of glucose to ten of gallic acid. Fischer concluded that the substance was penta m-digalloyl glucose, which he subsequently synthesized.

The product appeared qualitatively and quantitatively rather similar to the substance obtained from Chinese Nutgalls, but since both were amorphous the comparison was not too valid. Natural specimens seldom contain as much sugar as the formula requires, but this was attributed to the fact that there is always some free sugar, gallic, digallic and ellagic acids present. The low sugar content was believed to be due to the ease of hydrolysis during purification.

In 1921 Nierenstein, Spiers and Geake [4] showed that methylated gallotannin gave tetramethyl glucose on hydrolysis whereas Fischer's methylated synthetic penta-digalloyl glucose gave glucose under the same conditions. From this it appeared that in the gallotannin glucoside all the gallic acid residues were linked together and attached by one of them to carbon atom number one of glucose. Such a conclusion, however, would be weakened if the gallotannin contained free glucose before methylation.

In 1926 Nierenstein [4] stated, "I do *not* regard glucose as an essential part of the gallotannin molecule, since we have found that by the action of yeast it is possible to free gallotannin from glucose *without destroying the gallotannin molecule*. The view held by me is: gallotannin is a poly-digalloyl leuco digallic acid anhydride as originally suggested by me in 1912, which may or may not exist in the form of a glucoside, to which we have assigned the name gallotannin-glucoside. The fact that gallotannin may be freed from glucose by the action of yeast finally disposes of the penta-digalloyl-glucose formula of Fischer as opposed to my views of gallotannin."

Mitchell [5] originally supported the Fischer formula, but changed over to support of the Nierenstein formula on analytical considerations. Hoesch [6], however, considered leuco-m-digallic acid to have been invented by Nierenstein.

In 1951 Schmidt and Lademann [7] investigated gallotannins and their fission products by paper chromatography. In some cases the Rf values did not permit differentiation between the tannins but they could often be distinguished by color tests. No mention was made of prior purification of the tannins.

B. Ellagitannins

Certain tannins such as valonia (from the acorns of Turkish oak, *Quercus aegilops*) produce a "bloom" or surface coating on leather. This same deposit appears when solutions of myrobalans (the dried nuts of *Terminalia chebula*), dividivi (the pods of *Caesalpinia coriaria*, Willd.), oak bark, etc. are left

standing. This substance has been identified as ellagic acid by Nierenstein by its analysis and by analysis of its tetracetate [8].

Löwe [9], Trimble [10], Bjalobresheski [11], and Perkin [12] felt that ellagitannins were glucosides of ellagic acid but such glucosides were not found in the bloom producing tannins. Perkins and Nierenstein [13] thought that ellagitannins were galloyl derivatives of ellagic acid. The latter [14] synthesized tetragalloyl ellagic acid and showed that it precipitated gelatin.

Nierenstein [15] crystallized the ellagitannin from myrobalans and hydrolyzed it with emulsin to luteoic acid and two molecules of glucose. By loss of a water molecule luteoic acid would yield ellagic acid thus accounting for the "bloom" produced by myrobalans.

1. *Chebulinic Acid from Myrobalans*

According to Nierenstein myrobalans contains a number of substances among which are included myrobalani-tannin and chebulinic acid. He considers myrobalani-tannin to be an ellagitannin and obtained it in crystalline form [15] as previously mentioned. Myrobalans contain 27.3 – 33.0 per cent tannin [16]. Nierenstein recently found 21.2 per cent of his crystalline luteoic acid 5-biglucoside in *Terminalia chebula*, Retz [17]. It gave on analysis by the hide powder method an average value of 99.1 per cent tannin.

He considered chebulinic acid to be only a by-product and not the main tannin in *Terminalia chebula* [18]. There was some confusion in the early work between chebulinic acid and myrobalani-tannin. Following the early work, Fischer and Freudenberg [19] found that chebulinic acid yielded glucose on hydrolysis. This acid exists to the extent of 4 per cent in myrobalans [20]. Freudenberg and Fick [21] found that chebulinic acid was a digalloyl glucose linked to an acid of formula, $C_{13}H_{12}O_9$ COOH. In 1927 Freudenberg and Frank [22] hydrolyzed chebulinic acid, $C_{41}H_{34}O_{27}.9H_2O$, to give three moles of gallic acid, one mole of glucose and one mole of the previously found fission acid.

2. *Chebulagic Acid from Myrobalans*

In 1947 Schmidt and co-workers [23] reported on a careful study of chebulinic acid from myrobalans. This was followed with the announcement [24] of the isolation of another crystalline product, an ellagitannin, chebulagic acid, $C_{41}H_{30}O_{27}.10H_2O$, in 1-2 per cent yield, from the same source. Complete hydrolysis of chebulagic acid gave one mole each of ellagic acid, gallic acid, glucose and fission acid, $C_{14}H_{12}O_{11}$. The latter is the same acid as that obtained from chebulinic acid. It has been assigned a slightly different formula from that previously given which is now based on the analyses of crystalline derivatives.

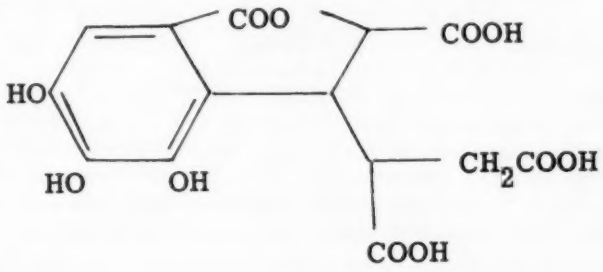
3. *Dividivi Tannin*

Nierenstein [18], (p. 194) investigated dividivi tannin (*Caesalpinia coriaria*) and found it to be amorphous. On hydrolysis with tannase he isolated ellagic acid, gallic acid, the fission acid previously obtained from myrobalans and a small quantity of glucose. The small quantity of glucose caused Nierenstein to consider that it was not part of the tannin molecule and that the tannin consisted of the fission acid, ellagic acid and gallic acid. Later he was able to isolate 14.3 per cent luteoic acid 5-biglucoside [17] which he also found in myrobalans. Dividivi itself contains a total of 40–45 per cent tannins based on the weight of the dried pods [16], (p. 50).

In 1950 Schmidt and Lademann [25] isolated from dividivi about 2.5 per cent of crystalline acid which was identical with the chebulagic acid previously obtained from myrobalans. On hydrolysis it gave the fission acid, ellagic acid, gallic acid and glucose. The latter was found in less than equimolar quantity.

4. *The Fission Acid*

An extensive study of the constitution of the fission acid obtained from chebulinic and chebulagic acids was carried out by Schmidt and Mayer [26] and the yield of trimethyl fission acid obtained from myrobalans was greatly improved [27]. The following structure was proposed:



It was given the designation "chebulic acid" [28].

5. *Digalloyl Glucose*

In 1919 Freudenberg [29] reported the isolation of digalloyl glucose from chebulinic acid together with one mole of gallic acid and one mole of fission (chebulic) acid. Recent studies by Schmidt and co-workers [30, 31] have proved the digalloyl glucose to be 3,6 digalloyl glucose and identical with the synthetic product.

6. *Corilagin*

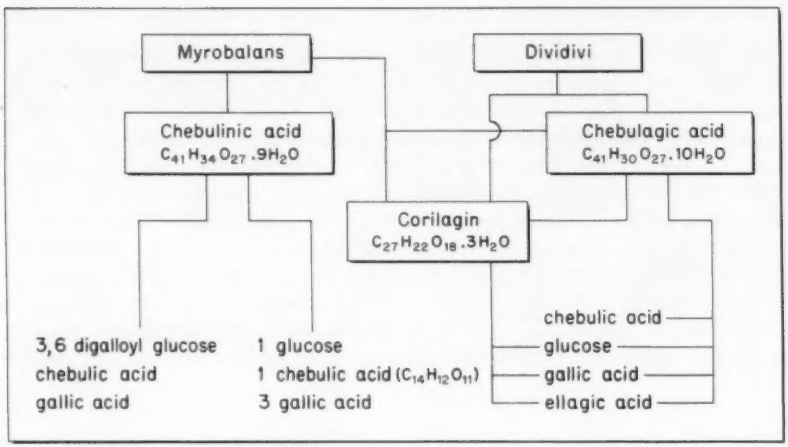
Schmidt and Lademann[32] have recently isolated another crystalline tannin, corilagin, $C_{27}H_{22}O_{18}.3H_2O$, from dividivi. On hydrolysis it gave equimolar quantities of ellagic acid, gallic acid and glucose.

The methylated derivatives of both corilagin and chebulagic acid on hydrolysis gave optically active hexamethoxydiphenic acid[33]. The latter was subsequently synthesized[34]. This discovery by Schmidt and Blinn[35] appears to be the first case of stereoisomerism of a natural product due to hindered rotation.

Very recently Schmidt and Schmidt have shown that chebulagic acid may be hydrolyzed under mild conditions to corilagin and chebulic acid[36]. They have also shown that corilagin exists free in myrobalans[37].

7. *Summary*

The preceding discussion of modern work on ellagitannins is outlined below:



C. Chestnut Tannin

The three common species of chestnut are *Castanea dentata*, *Castanea vesca*, and *Castanea sativa*. Botanists are not in agreement as to the identiy of these species, therefore, the value of much of the work done on chestnut tannin is difficult to assess. Some workers have not specified the botanical name of the species used in their investigations. Others have worked on the tannin obtained from the horse chestnut tree, *Aesculus hippocastanum*, which is not a true chestnut.

Trimble[38] investigated in 1891 a substance isolated from the wood of *Castanea vesca*. He purified the material by solvent extraction and fractional precipitation with lead oxyacetate and obtained a nearly white porous solid which decomposed above 200°C. to give pyrogallic and metagallic acids. On the basis of a series of qualitative tests and by adjusting his analytical figures to allow for the presence of sugar, he concluded that chestnutwood tannin was identical with gallotannin.

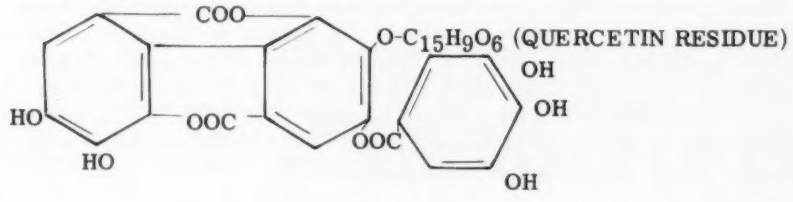
In 1921 Freudenberg and Walpuski[39], also working with tannin from the wood of *Castanea vesca*, purified the crude material by lead salt methods to obtain "raw" tannin. This substance gave 15–20 per cent ellagic acid and traces of gallic acid, sugar, and quercetin on acid hydrolysis. An attempted hydrolysis with emulsin gave no sugar.

When a quantity of the "raw" tannin was treated with Aspergillus niger a 31 per cent yield of "pure" tannin was isolated which was free of nitrogen and was not hydrolysable. Titration with sodium hydroxide indicated a molecular weight of 400 or a multiple thereof. The tannin gave a blue color with iron salts and formed no precipitate with bromine water.

In 1927 Kurmeier[40] obtained a tannin from the leaves of *Castanea Vesca* to which he assigned the formula $C_{24}H_{20}O_{16}$. To obtain this he treated a freshly extracted tannin solution with a lead salt, filtered and washed the lead tannate, and decomposed it with sulfuric acid. Condensation products were then removed from a dilute solution of the tannin by precipitation with pyridine. The tannin was recovered from the pyridine-water solution by a second lead salt precipitation. Decomposition with sulfuric acid and precipitation with quinoline gave the purified tannin. This material had a rotation $[\alpha]_D$ in water of −16° (±8°). Methylation with diazomethane gave an amorphous yellow solid $C_{24}H_{12}O_8$ $(OCH_3)_8$, which exhibited a rotation of −37° in acetone and −35° in methanol. A molecular weight determination of the methylated derivative gave values of 676 in benzene and 650 and 623 in ethylene bromide. The action of tannase, as well as acid and alkaline hydrolysis, gave ellagic acid in amounts varying from 8 to 17 per cent.

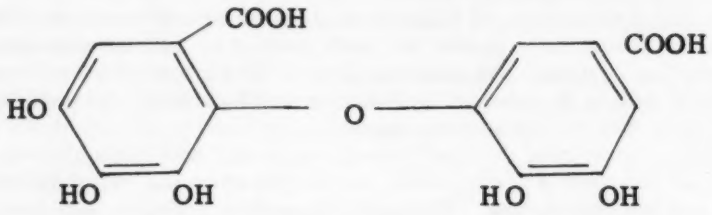
Another hydrolysis of chestnutwood tannin was reported by Nass[41] to yield ellagic acid, gallic acid, and glucose. Curtius and Franzen[42] also found ellagic acid.

Nierenstein[18], (p. 191) summarized the data on chestnutwood tannin through 1934 and proposed the following formula:



There is no evidence to support this formula other than the presence of gallic acid, ellagic acid, and quercetin among the hydrolysis products of Freudenberg's "raw" tannin.

Mayer[43] recently reported the isolation of a crystalline compound having tanning properties from young chestnut leaves. He established the following structure for this dehydrodigallic acid.



Clark and Levy[44], as well as Buchanan and co-workers[45] attempted to purify crude chestnut extract. The former succeeded in fractionating a solution of the tannin on a Solka Floc column. They achieved a partial separation into six constituents and demonstrated that further purification could be achieved by refractionation of one of the main bands. Buchanan obtained a specimen of chestnut tannin having a purity of 96 per cent by the A.L.C.A. method of tannin analysis. The yield was 12 per cent.

In 1943 Sourlangas[46] published data on the acid nature of pyrogallol tannins. He titrated an ether-extracted chestnut tannin with base and concluded that there were indications of a free carboxyl group in the tannin molecule. No purification of the crude extract was made.

Douglas and Humphreys[47] determined the molecular weight of chestnut tannin before and after electrodialysis. The initial value, 462, was increased to 1545 by this treatment.

In 1947 Schmidt and Hüll[48] isolated d-catechin from chestnut shells, *Castanea vesca*, in 0.6 per cent yield.

Table I summarizes the analytical data obtained by the several investigators.

Discussion of Experimental Work

Crude chestnut extract from *Castanea dentata* was obtained from the Texas Extract Company, Nashville, Tennessee. It gave a green color reaction when warmed with sodium nitrite in Procter's test for ellagi-tannins. It gave a red color when dilute hydrochloric acid was added. It liberated iodine from a solution of iodic acid, gave a blue-black color with ferric chloride and a yellow color with concentrated sulfuric acid. It gave no precipitate with bromine water. Sodium sulfite gave a red solution[49].

TABLE I

Worker	Botanical Species	Section of tree
a. Trimble [38]	*Castanea vesca*	wood
b. Freudenberg [39]	*Castanea vesca*	wood
c. Kurmeier [40]	*Castanea vesca*	leaves
d. Buchanan [45]	Not specified	wood
e. Nierenstein [18], (p. 191)	Not specified	wood
f. Mayer (43)	*Castanea vesca*	leaves & twigs

	C	H	N	MeO	Ash	M.W.	Formula
a.	51.15	4.58	——	——	——	——	$C_{14}H_{10}O_9$
a.	50.95	4.79	——	——	——	——	
b.	50.82	3.34					
b.	50.75	3.29	None	——	——	——	——
c.	49.84	3.95	——	——	——	650, 676	$C_{34}H_{20}O_{16}$
c.	50.13	3.84	——	——	——	623	
d.	53.4	4.0	0.20	2.8	0.32	——	——
e.	——	——	——	——	——	——	$C_{28}H_{18}O_{18}$
f.	49.80	3.03	——	——	——	——	$C_{14}H_{10}O_{10}$
f.	49.59	3.08	——	——	——	——	

In the commercial preparation of chestnut extract, the extraction of the wood is performed at 55–100°C. by the open leach process or at 55–130°C. by autoclaving. A 5 per cent solution of crude chestnut has a pH of about 2.6. This is equal to the pH of 0.006 M hydrochloric acid. It seems reasonable to assume that during a large part of the extraction the solution is subjected to an hydrolysis effect equivalent to that produced by 0.01 M hydrochloric acid under the time, temperature and pressure conditions employed. Before extraction the wood may contain free sugar, sugar free tannin and tannin bound sugar. After extraction possibly no sugar remains bound to tannin. As will subsequently be shown, a chestnut tannin sample freed of free sugars by lead salt and hydrogen sulfide treatment failed to give a test for sugars after hydrolysis with sulfuric acid.

If some ellagic acid exists in the form of an easily hydrolyzed glycoside in the original chestnut wood it may be hydrolyzed in the process of extraction of the tannin and the free ellagic acid largely removed when the spent wood is removed.

A. *Preparation of Extract A*

In our initial studies the crude extract was dissolved in a mixture of acetone and water, filtered and evaporated. The residue was dissolved in water and precipitated as the lead salt. After filtration and washing the salt was decomposed with hydrogen sulfide. Following recovery of the tannin, it was dissolved in methanol, filtered, and the tannin precipitated with ether.

The solid was treated with ethyl acetate and filtered, the residue being retained. The latter was extracted with isopropyl alcohol, and the solid tannin recovered from the solution giving Extract A.

B. *Hydrolytic Studies*

The following methods were employed in various attempts to obtain information concerning the presence or absence of a sugar residue on the tannin molecule. Extract A was used for the following experiments.

1. Hydrolysis with 5 per cent hydrochloric acid for fifteen minutes on a steam bath.
2. Treatment with an absolute ethanol solution of sodium ethoxide for three days at room temperature.
3. Hydrolysis by refluxing with 5 per cent sodium hydroxide for three and one-half hours.
4. Hydrolysis by refluxing with 10 per cent sodium hydroxide for five hours.
5. Refluxing with potassium hydroxide for two hours.
6. Refluxing with glacial acetic acid for two hours.
7. Refluxing with pyridine for two and one-half hours.
8. Seven days standing at room temperature in methanol solution containing dissolved hydrogen chloride.
9. Refluxing for three and one-half hours with 5 per cent sulfuric acid.
10. Hydrolysis with emulsin.

The treatment of the reaction mixture varied widely with the procedure used. In all cases, an aqueous solution of water solubles was eventually obtained. This was neutralized, decolorized if possible, and tested with Fehling's solution, the Molisch reagent, and phenylhydrazine.

Decolorization was effected either with Norit, or by precipitation of the tannin with lead acetate. After filtration the water solution was treated with hydrogen sulfide to precipitate excess lead as lead sulfide. After neutralization with sodium carbonate, the last traces of color were removed with Norit; and the clear filtrate, after concentration at reduced pressure, was tested with the several sugar reagents.

It was found that use of the anthrone reagent [50] as a test for carbohydrates was more effective than the Molisch test. Positive tests with anthrone reagent were obtained both with sugars and glycosides (naringin and phloridzin).

The tests indicated that no sugars were released by the hydrolysis and that no glycosides were present.

C. *Preparation of Extracts B, C, and D*

In order to improve the analytical purity of the tannin and to increase the yield, new methods of purification were investigated. Among these considered and tried were:

1. Further solvent treatments
2. Precipitating agents
3. Ion exchange resins
4. Chromatographic columns

It was difficult to obtain clear-cut separations with many of the solvents tried. When other precipitating agents were tried, no improvement over the formation of the lead salt could be effected. A strongly alkaline ion-exchange resin oxidized the tannin but did not absorb it despite the latter's known acidity. Chromatographic columns showed some promise, but the difficulties involved in constructing a cellulose column and in obtaining the purified product in quantity acted as a deterrent to the employment of this method. A liquid-liquid purification employing different pH values was investigated and showed promise, but suitable equipment was not at hand. Counter current studies were made and some fractionation was achieved, but a more elaborate and expensive apparatus than was employed would be required to obtain a quantity of purified tannin.

A consistent set of formulas for the several purified extracts could be devised only after assuming the presence of water of crystallization in the samples dried at 100°C. (vac.) for analysis. Since a portion of the sample analyzed for the elements could not conveniently be obtained under the same conditions at the same time for water analysis, this determination was not made.

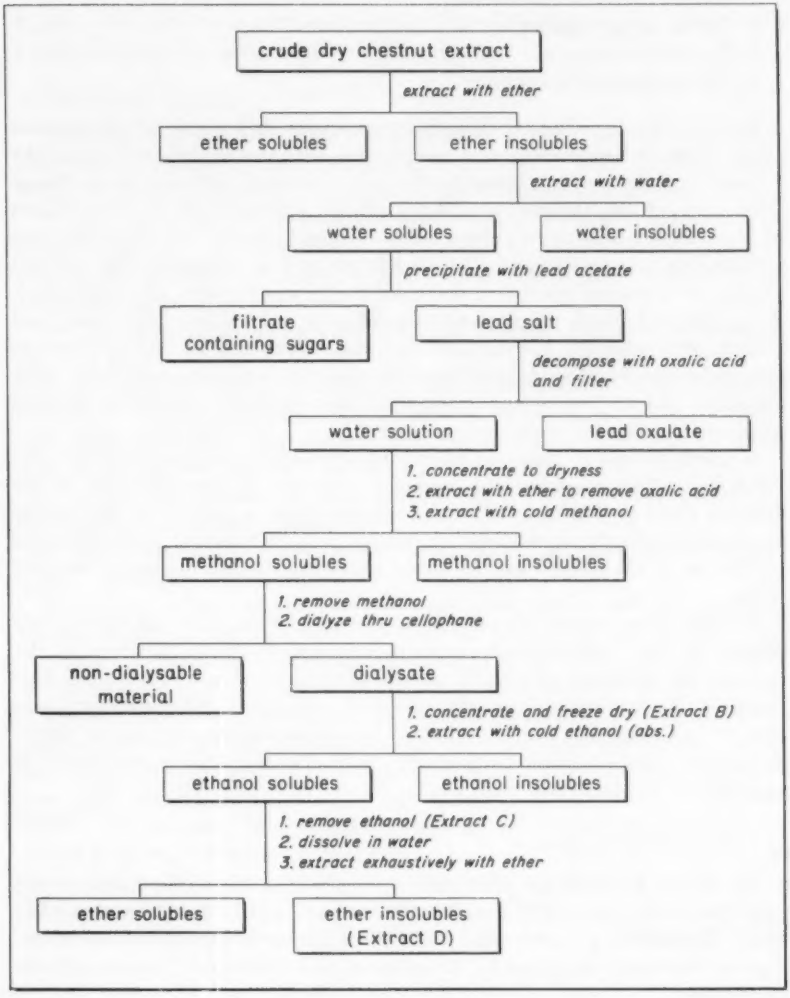
All efforts to remove the small amount of methoxyl (or alkoxyl) group present in the purified tannin extracts were unsuccessful. Analysis of the extracts for methoxyl at twenty minute intervals indicated that a small amount (0.3 per cent) continually appeared. Apparently the methoxyl was not present originally but was formed by decomposition during the determination. Further attempts to purify crude chestnut tannin were made as outlined in the chart on page 74.

D. *Crude Extract Sugars*

The aqueous filtrate left after removal of the lead salt of the tannin in the preparation of chestnut Extract B was investigated. A chromatographic study showed the presence of at least seven sugars or sugar-like substances. Two of these were identified by Rf values in two different solvents as glucose and xylose.

E. *Titration Studies*

The next series of experiments consisted of titrations of the various purified chestnut extracts in water or methanol. They failed to give satisfactory titration curves presumably due to the number of phenolic hydroxyl groups present. No carboxyl group appeared to be present.



F. *Alkaline Fusion of Extract B*

Extract B was examined for the possible presence of starch and free gallic acid. They were found to be absent. Alkali fusion of the extract produced a small quantity of gallic acid.

G. *Extract B Compared with Gallotannin*

Oxidation by air in alkaline solution and by hydrogen peroxide in water of Extract B failed to form ellagic acid whereas the same procedures applied to tannic acid (gallotannin) were successful. Thus, chestnut tannin is clearly distinguished from gallotannin. It will subsequently be shown that chestnut tannin does yield ellagic acid in acid solution and also by the action of an enzyme.

H. *Extracts C and D*

Extract B was further purified (See chart) by ethanol extraction to reduce ash. This product was Extract C and was the chestnut extract employed in making the physical measurements in article VI of this series[51]. A lengthy ether extraction of a water solution of the extract was the last step in the purification. This gave Substance D.

It has been noticed previously that the aqueous solution obtained in the dialysis step developed a mold growth on standing and deposited crystals. The latter were identified as ellagic acid by chemical analysis, infra-red spectrogram and X-ray diffraction diagram. Prior to the final ether extraction ellagic acid could be detected as an impurity in the chestnut extract by paper ionophoresis. The ether extraction completely eliminated the ellagic acid and thus Substance D did not contain this contaminant. The action of an enzyme on Substance D formed ellagic acid as shown by paper ionophoresis. This proved for the first time that chestnut tannin completely freed of uncombined ellagic acid formed the latter and hence that it is a constituent part of the tannin molecule.

I. *Chromatography and Ionophoresis*

A series of chromatographic studies of the purified chestnut tannin extracts were carried out. The usual solvent combinations failed to move the tannin or ellagic acid, although phenolic acids are easily chromatographed. Thus, the absence of the latter was easily demonstrated. Solvents buffered to an alkaline pH value gave Rf values for phlobatannins but the chestnut extracts gave continuous streaks. Paper ionophoresis of Extract D at pH $= 8$ and 10 gave satisfactory mobilities of 18.2×10^{-5} and 18.9×10^{-5} cm^2/volt-sec. respectively. The ionograms indicated the absence of free ellagic acid since its mobility had been determined. No coloring matters could be detected. A very weak blue fluorescence appeared close to the tannin area.

J. *Absorption Spectra*

An ultraviolet spectogram of Extract D was obtained in the region 230–435 mμ. No peaks appeared. This is in accord with the observation of Buchanan, Lewis and Weber[45] on chestnut extract.

Infra-red spectrograms of the various chestnut fractions were prepared. All the chestnut fractions showed a strong keto absorption.

Experimental

Purification of Substance A

Two kilograms of the extract was dissolved in a mixture of 7 liters of acetone and 5400 ml. of water. The solution was filtered and the filtrate concentrated to dryness on a steam bath. A yield of 1734 grams of soluble material was obtained.

One-hundred grams of the acetone-water soluble material was dissolved in three liters of water. A 10 per cent lead acetate solution (368 ml.) was then added in a dropwise fashion with stirring. The light brown precipitate of lead tannate was collected by suction filtration and the clear yellow solution containing sugars was set aside. The lead tannate was thoroughly washed with distilled water and finally suspended in four liters of water. Hydrogen sulfide was bubbled through the suspension with vigorous stirring. To free the mixture from hydrogen sulfide, nitrogen was bubbled through for one hour with continued stirring. The solution was then heated for one hour on the steam bath, a quantity of filtering aid (Si-o-lite) was added, and the mixture filtered. The clear filtrate was evaporated to dryness on a steam bath to give a brown solid. The total yield of this material was 701 grams from 2000 grams of crude extract.

One-hundred grams of this material was rotated in a bottle with two liters of absolute methanol for seven hours. The methanol filtrate was concentrated to 200 ml. by distillation at reduced pressure, cooled, and added with stirring to six volumes of absolute ether. The light brown solid which separated was collected by suction filtration and thoroughly washed with ether. The yield of this material was 520 grams from 2000 grams of crude extract.

A Soxhlet extraction of the methanol soluble material with ethyl acetate removed 6 per cent ethyl acetate-soluble material leaving 500 grams of tannin.

A 354 hour Soxhlet extraction of this material with isopropyl alcohol gave 263 grams of soluble material (Substance A). The yield of this material, based on 2000 grams of crude extract was 13 per cent.

Substance A had no definite melting point but decomposed above 200°C. It gave a blue-green color with ferric chloride and a precipitate with gelatin-salt solution.

Purification of Substance B

One-thousand grams of dry, powdered chestnut extract was placed in a Soxhlet apparatus and extracted with absolute ether for one week. This

treatment removed less than ten grams of resinous material. The ether insoluble material was then dissolved in thirty liters of distilled water and centrifuged. Ninety-eight grams of water insoluble material were removed by this treatment.

The lead salt of the tannin was next precipitated from the water solution by addition of 3300 ml. of 10 per cent lead acetate (neutral) solution. The brown salt which precipitated was collected by centrifugation and washed three times by trituration with water. It was then suspended in 27 liters of water and 315 grams of oxalic acid was added with vigorous stirring. After four hours the precipitate of lead oxalate was removed by filtration and the tannin solution concentrated to 2300 ml. by distillation at reduced pressure. The concentrate was then freeze-dried to a brown solid. This was exhaustively extracted with ether to remove residual oxalic acid. The weight of light brown material recovered was 542 grams.

The above material was rotated in bottles with excess methanol until no further solution occurred. Concentration of the methanol-soluble portion to dryness at reduced pressure gave 515 grams of brown solid.

This material was dissolved in 10.5 liters of distilled water and placed in cellophane tubes having a wall thickness of 0.0018 inches. These tubes were tied off and suspended in 125 liters of distilled water in covered jars. After 21 days the outside liquor was replaced with fresh distilled water. In another 21 days the dialysis was halted and the outside liquors were combined and concentrated to a volume of 1250 ml. by distillation at reduced pressure. Freeze-drying this concentrate gave a yellow-brown solid weighing 422 grams (Substance B).

Investigation of Lead Salt Filtrates

One-hundred grams of crude dry chestnut extract was dissolved in two liters of water. A 20 per cent solution of lead acetate was added to the tannin solution with stirring until no further precipitation was observed. Filtration removed the lead tannate and left a clear yellow solution. This was concentrated to 200 ml., filtered through a mat of celite to remove suspended materials, and freeze-dried. The yellow powder obtained was extracted exhaustively with ether to remove a small amount of yellow material.

The ether-insolubles were next exhaustively extracted with acetone which removed some gummy material.

The ether, acetone insoluble material was dissolved in water and treated with oxalic acid solution until no further precipitation was noted. Filtration afforded a clear yellow filtrate which was freeze-dried. Exhaustive ether extraction of the resulting solid removed excess oxalic acid and left 13.0 grams

of light yellow solid. When one gram of this material was exhaustively extracted with absolute methanol, there was obtained 0.35 grams of pure white solid (Substance A1).

This material was investigated further by the use of paper chromatography. All chromatograms were run on Whatman #11 paper using the solvent descent technique.

1. Because of the extremely low Rf values of the components of Substance A1, a series of chromatograms were run in which the solvent front was allowed to run off the end of the paper and the distance of travel of the several spots measured in centimeters.

Butanol: acetic acid: water (4:1:5) was employed for this series. An aniline hydrogen phthalate [52] spray was used to develop the chromatograms.

Component Number	Distance of travel in 50 hours (cm.)			Color with Spray
	a	b	c	
1	0.0	0.0	0.0	brown
2	1.9	1.1	1.7	brown
3	5.0	3.8	4.3	pink
4	12.0	11.0	10.6	pink
5	18.8	17.0	16.7	brown
6	22.9	22.2	21.2	pink
7	25.4	25.3	23.7	pink

2. Pyridine: ethyl acetate: water (2:4:4) was used in this 23.5 hour run. The spray was again aniline hydrogen phthalate.

Substance	Centimeters of travel	Centimeters of travel	Color with Spray
Al	5.2	10.4	brown
glucose	5.1		brown
xylose		10.4	brown

3. These chromatograms were run under the usual conditions using butanol: acetic acid: water (4:1:5). Aniline hydrogen phthalate was again used as a spray and normal Rf values were measured.

Substance	R_f	R_f	Color with Spray
Al	.15	.23	brown
glucose	.15		brown
xylose		.24	brown

First Fusion of Substance B

Ten grams of Substance B were dissolved in a mixture of 50 grams of sodium hydroxide and 50 ml. of water in a casserole. Five grams of zinc dust were added and the mixture boiled slowly for twenty minutes. The dark brown solution was allowed to cool, diluted with 100 ml. of water and filtered through a sintered glass funnel. The filtrate was chilled and acidified by dropwise addition of concentrated hydrochloric acid. A dark brown solid was removed by filtration and the filtrate exhaustively extracted with ether. The yellow ether solution was concentrated to 50 ml. and treated with 50 ml. of benzene. Cooling gave no precipitate. The ether was removed by distillation and the benzene solution extracted with water. A chromatogram of the water solution was run.

Solvent: butanol, acetic acid, water (4:1:5)

Paper: Whatman #11

Running time: 17 hours

Spray: Bis-diazotized benzidine [53]

The water solution showed a blue fluorescent spot at Rf = .24 and an orange spot at Rf .58. Known gallic acid gave an orange spot at Rf .58 on the same paper.

Second Fusion of Substance B

A mixture of 4 grams of Substance B, 5 grams of zinc dust, 35 grams of sodium hydroxide, and 35 ml. of water was gently boiled in a casserole for 15 minutes. The melt was cooled, diluted with water, and filtered. Ice was added to the filtrate which was then acidified with concentrated hydrochloric acid. The acid solution was extracted with five 200 ml. portions of ether and the ether solution dried over magnesium sulfate, filtered and concentrated to dryness at reduced pressure. A light brown powder was obtained which weighed 0.25 gram. When attempts to purify this material failed, a chromatogram was run on Whatman #11 paper using butanol: acetic acid: water (4:1:5). After 18 hours the chromatogram was dried and sprayed with a 2 per cent ferric chloride solution. The only definite spot developed was blue with an Rf = .60. Known gallic acid run on the same paper gave a blue color with ferric chloride solution and had an Rf = .60.

A small amount of the brown substance was placed in a test tube with 2 ml. of water. A few crystals of KCN were added and a red color appeared. This color faded on standing and was renewed on shaking. This test is characteristic of gallic acid.

First Oxidation of Tannic Acid

Twenty-five grams of tannic acid (Eastman Kodak Company, white label) were dissolved in 2.5 liters of 0.5 N sodium bicarbonate solution and placed in a five liter flask. Air was bubbled into the solution for 13 hours. Filtration afforded 3 grams of brown solid. This solid was dissolved in 0.1 *N* sodium hydroxide, filtered to remove some insoluble matter and the filtrate acidified with dilute sulfuric acid. The resulting precipitate was collected, dried, and crystallized from pyridine. Yellow needles were obtained which were boiled with water for one hour, filtered, and washed to give a faintly yellow microcrystalline compound. This material was identical with synthetic ellagic acid according to its infra-red spectogram.

Second Oxidation of Tannic Acid

Fifteen grams of tannic acid (Eastman Kodak Company, white label) was dissolved in 250 ml. of water in a 500 ml. flask. Ten ml. of 30 per cent hydrogen peroxide solution were added and the mixture refluxed for two hours. After cooling the solution was filtered to obtain 3 grams of brown solid which was washed with water and dissolved in 1 *N* sodium hydroxide. After filtration excess carbon dioxide was bubbled into the solution giving a yellow precipitate. This substance was recrystallized from pyridine and the pyridine salt boiled with water. Filtration yielded a very faintly yellow microcrystalline solid which gave a positive Griessmayer test[54] for ellagic acid and was identical with synthetic ellagic acid according to its infra-red spectrogram.

Oxidation of Substance B

The above experiments, using air oxidation in an alkaline medium and hydrogen peroxide oxidation were repeated using Substance B in place of tannic acid. In neither case was any ellagic acid obtained.

Purification of Substance C

In an attempt to reduce the ash content of Substance B, the following further purification was introduced.

One gram of Substance B was thoroughly dried and extracted with excess warm absolute ethanol. The solution was filtered and concentrated to dryness at reduced pressure. The residue was taken up in 100 ml. of absolute ethanol, filtered and the filtrate concentrated to dryness at reduced pressure. The residue was dissolved in 20 ml. of water, heated to drive off residual ethanol, filtered and the filtrate freeze-dried. A 95 per cent yield of ethanol soluble material was obtained (Substance C).

Found: Substance C

C	H	MeO	Acetyl	Ash
52.56	3.96	3.13	7.38	trace
52.30	4.03	3.22	7.50	trace

Purification of Substance D

Substance C (7.8 grams) was dissolved in 100 ml. of water and extracted in a liquid-liquid extractor with ether for 163 hours. At the end of this period no ellagic acid could be detected in the aqueous solution by paper ionophoresis.

An extremely sensitive test for ellagic acid consists of spraying the chromatogram with alkaline buffer solution (pH = 8-10). Under these conditions ellagic acid exhibits a blue fluorescence and a green phosphorescence under ultra-violet light. The duration of phosphorescence varies with the concentration of ellagic acid.

The aqueous solution was concentrated to 50 ml. at reduced pressure and freeze-dried. A yield of 6.0 grams (77 per cent) of brown solid was obtained (Substance D).

Found: Substance D

C	H	MeO	Acetyl	Ash	N
51.60	3.87	1.93	None	0.26	Trace
51.89	3.63	2.19	None	0.56	

The ether extracts were combined and evaporated to dryness. The brown residue was taken up in 100 ml. of hot ethanol and filtered. Two volumes of water were added to the filtrate causing eventual deposition of a brown solid. This solid was collected by filtration and washed with water. It gave a positive Griessmayer test[54] for ellagic acid and when recrystallized from pyridine gave a yellow crystalline material. Boiling this material with water gave 58 mg. of substance which was identical with synthetic ellagic acid.

Ellagic Acid from Substance B

Mold growth was observed on the surface of a solution of 80 grams of Substance B in 20 liters of distilled water which had been standing in a covered jar for three months. Filtration of the solution gave a brown substance which was washed with water and dried at 110°C. The dried solids were extracted with boiling pyridine and the pyridine solution filtered. Cooling gave yellow needle-like crystals which were collected, boiled with water, and filtered to give a faintly yellow microcrystalline solid weighing 1.5 grams. This solid was found to be identical with ellagic acid by infra-red spectro-

gram and melting point behaviour. Both known ellagic acid and the isolated solid decompose above 360°C. The material also gave the Griessmayer test.[54]

A sample of the material was again recrystallized from pyridine to give yellow needles. The pyridine salt was boiled with a large volume of absolute ethanol and filtered. Addition of one volume of water to the ethanol filtrate and then allowing the solution to stand for 24 hours gave a white microcrystalline solid which was analyzed (Substance B1).

Sample dried to constant weight at 160°C. (vac.)

Found

C	H
55.4	2.4
55.4	2.3

Calc.
$C_{14}H_6O_8$

C	H
55.6	2.0

X-ray diffraction patterns of Substance B1 and synthetic ellagic acid, kindly prepared by Dr. R. E. Dreikorn, confirmed their identity.

Identification of Mold

A sample of the mold obtained from the water solution of Substance B was serially diluted and plated out on Czapek's medium. A single colony was cultivated on a slant of Czapek's medium and examined microscopically. It appeared to be identical to a known specimen of Aspergillus Niger.

This work was carried out under the direction of Dr. T. D. Kroner (these laboratories).

Enzymatic Hydrolysis

a. *Preparation of Tannase*

Two liters of Czapek's medium was prepared[55] and adjusted to pH = 5 with 2 *N* hydrochloric acid. Two hundred and fifty ml. of this solution was placed in each of 6 one liter flasks stoppered with cotton. The solutions were sterilized in an autoclave at 15 pounds pressure for 20 minutes, then innoculated with Aspergillus Niger. The flasks were incubated at 25°C. for seven days when the mold was separated by decantation and washed with water. The damp mold was cut into small pieces and suspended in 500 ml. of water

to which were added two ml. of toluene. After 30 hours the solution was filtered and the filtrate freeze-dried. The dry solid was washed with ethanol and dried in air to give one gram of yellow solid. The yellow solid was dissolved in a small amount of water and precipitated by dropping into 10 volumes of absolute ethanol. Filtration and drying gave an almost white powder which was used for the following hydrolyses.

b. *Hydrolysis*

Two grams of Substance D was dissolved in 400 ml. of distilled water. The pH was adjusted to 5.0 with ammonium hydroxide. Tannase (0.1 g.) was added and the flask was incubated for two weeks at 28°C.

After acidifying to pH = 1.5 with hydrochloric acid, the aqueous solution was extracted with ether in a liquid-liquid extractor. After two hours extraction ellagic acid was detected in the ether solution. Sufficient amounts for analysis were not obtained, but chromatograms of ether extract showed the characteristic ellagic acid streaks from the origin of Rf ca. 0.1. These areas phosphoresced green after exposure to ultra-violet light.

Ionophoresis

Paper ionograms of Substance C and Substance D were prepared according to the same procedure used by Putnam and Bowles in Article VIII of this series. Substance C, run at pH = 8, showed a blue fluorescent area which phosphoresced green and had a mobility circa 5.0×10^{-5} cm²/volt-sec. Known ellagic acid run under the same conditions showed the same fluorescence characteristics and mobility. Substance D showed no ellagic acid spot. Its mobilities were 18.2×10^{-5} and 18.9×10^{-5} cm²/volt-sec. at pH = 8 and pH = 10 respectively.

Ultra-violet Spectra

Ultra-violet spectrograms of Substance D were run in the region 230-435 mμ. Absolute ethanol solutions of 0.001 and 0.01 per cent concentrations were employed. Measurements were taken on a Beckman spectrophotometer, Model DU.

No maxima were observed.

Infra-Red Spectra

All infra-red spectrograms were run on a Perkin-Elmer double beam infra-red recording spectrophotometer, Model 21. The tannin extracts and ellagic acids were run in nujol. All the chestnut fractions showed a strong keto absorption.

Summary

1. The crude extract was found to contain at least seven sugars of which two were identified as glucose and xylose.

2. Hydrolytic studies failed to reveal the presence of any sugars as components of the purified tannin.

3. Oxidation experiments which succeeded in producing ellagic acid from gallotannin, failed with chestnut tannin thus distinguishing between them.

4. Ionophoretic studies were carried out and the mobility of the tannin determined. This method was used to demonstrate the complete removal of free ellagic acid from the tannin.

5. Tannin completely free of ellagic acid formed the latter by enzymic hydrolysis.

6. The infra-red spectrogram of the tannin showed a strong keto absorption.

7. Alkaline fusion of the tannin produced a very small amount of gallic acid.

Bibliography

1. Perkin and Everest, The Natural Organic Colouring Matters, Longmans, N. Y. (1918)
2. Freudenberg, Die Chemie der naturlichen Gerbstoffe, p. 4, Springer, Berlin (1920).
3. Fischer, Untersuchungen uber Depside and Gerbstoffe, Springer, Berlin (1920).
4. Nierenstein, Spiers and Geake, *J. Chem. Soc.* **119,** 284 (1921).
5. Mitchell, *Analyst* **48,** 2 (1923).
6. Hoesch, Emil Fischer, Sein Leben und Sein Werk . . .p. 466, "Verlag Chemie", Berlin (1921).
7. Schmidt and Lademann, *Ann.* **571,** 41 (1951).
8. Nierenstein, *Chem. Zt.* p. 87 (1909).
9. Löwe, *Z. anal. Chem.* **14,** 40 (1876).
10. Trimble, The Tannins **1,** 27 (1891) Phila.
11. Bjalobresheski, *Pharm.* **22,** 3 (1900).
12. Perkin and Gunnell, *J. Chem. Soc.* **69,** 1303 (1896).
13. Perkin and Nierenstein, *J. Chem. Soc.* **87,** 1412 (1905).
14. Nierenstein, *Ber.* **44,** 837 (1911).
15. Nierenstein, *Ber.* **43,** 1267 (1910).
16. Nierenstein, Allen's Commercial Organic Analysis, Fifth Ed., Vol. 5 p. 53, Blakiston, Phila. (1948).
17. Nierenstein and Potter, *Biochem. J.* **39,** 390 (1945).
18. Nierenstein, The Natural Organic Tannins, p. 198, Churchill, London (1934).
19. Fischer and Freudenberg, *Ber.* **45,** 918 (1912).
20. Passler and Hoffmann, *Ledertechn. Rundschau* p. 129 (1913).
21. Freudenberg and Fick, *Ber.* **53,** 1728 (1920).
22. Freudenberg and Frank, *Ann.* **452,** 303 (1927).
23. Schmidt, Heintzler and Mayer, *Ber.* **80,** 510 (1947).
24. Schmidt and Nieswandt, *Ann.* **568,** 165 (1950).
25. Schmidt and Lademann, *Ann.* **569,** 149 (1950).
26. Schmidt and Mayer, *Ann.* **571,** 1 (1951).
27. Mayer, *Ann.* **571,** 15 (1951).
28. Schmidt, Lademann and Himmele, *Ber.* **85,** 408 (1952).
29. Freudenberg, *Ber.* **52,** 1238 (1919).

30. Schmidt, Berg, and Baer, *Ann.* **571,** 19 (1951).
31. Schmidt and Schach, *Ann.* **571,** 29 (1951).
32. Schmidt and Lademann, *Ann.* **571,** 232 (1951).
33. Schmidt, Blinn and Lademann, *Ann.* **576,** 75 (1952).
34. Schmidt and Demmler, *Ann.* **576,** 85 (1952).
35. Schmidt and Blinn, *Naturwissenschaften,* **38,** 72 (1951).
36. Schmidt and Schmidt, *Ann.* **578,** 25 (1952).
37. Schmidt and Schmidt, *Ann.* **578,** 31 (1952).
38. Trimble, *J. Franklin Inst.* **132,** 303 (1891).
39. Freudenberg and Walpuski, *Ber.* **54,** 1695 (1921).
40. Kurmeir, *Collegium VI,* **273** (1927).
41. Nass, Ueber den Gerbstoff der Castanea vesca, Dorpat (1884).
42. Curtius and Franzen, *Sitzber. heidelberg Akad. Wiss. Math. naturw. Klasse* (1916).
43. Mayer, *Ann.* **578,** 34 (1952), Leder **2,** 277 (1951).
44. Clark and Levy, *J. Sci. Food Agr.* **1,** 213 (1950).
45. Buchanan, Lewis and Weber, *J. Am. Leather Chemists' Assoc.* **45,** 513 (1950).
46. Sourlangas and Atkin, *J. Intern. Soc. Leather Trades' Chemists* **27,** 183 (1943).
47. Douglas and Humphreys, *J. Intern. Soc. Leather Trades' Chemists* **21,** 378 (1937).
48. Schmidt and Hüll, *Ber.* **80,** 509 (1947).
49. Procter, *J. Soc. Chem. Ind.* (London) **13,** 487 (1894).
50. Morse, *Anal. Chem.* **19,** 1012 (1947).
51. Putnam, *J. Am. Leather Chemists' Assoc.* **48,** 125 (1953).
52. Partridge, *Nature* **164,** 443 (1949).
53. Koch and Krieg, *Chem. Ztg.* **62,** 140 (1938).
54. Griessmayer, *Ann.* **160,** 55 (1871).
55. Rockwell and O'Flaherty, *J. Am. Leather Chemists' Assoc.* **26,** 220 (1931).

Received, Sept. 8, 1954.

The Preparation and Tanning Properties of Phenolic Derivatives of Ligninsulfonic Acid: Part I*

H. Borden Marshall and Mary Krizsan

Ontario Research Foundation
Toronto, Canada

The importance of lignin as a potential tanning material has been widely recognized. The absence of any real tanning properties in lignin has been discussed by a number of investigators who are in general agreement that this is due to the relatively low ratio of phenolic hydroxyl groups.

Freudenberg [1] compared the structure of lignin with that of the natural tannins, and on the basis of this comparison has indicated the properties

*Presented at the Fiftieth Annual Meeting of The American Leather Chemists Association, Bedford Springs, Penn., June 7, 1954.

which contribute to, or detract from, its ability to produce a successful tannage. Tanning by ligninsulfonic acid was attributed to the presence of sulfonic and phenolic hydroxyl groups, although ligninsulfonic acid possesses a smaller percentage of the latter than the natural tanning agents. Penetration is favoured by the strongly polar character of the molecules and by the fact that molecules of all sizes are present. The secondary and tertiary hydroxyl groups also increase the solubility and penetration, but probably cause the undesirable hydrophylic character of leather tanned with ligninsulfonic acid alone.

Gustavson [2] likewise attributed the decreased hydrothermal stability of the hide, after treating with ligninsulfonic acid, to the structural peculiarities of the lignin molecule, such as the inadequate number of phenolic hydroxyl groups, rather than to the molecular size. He concluded that a chemical modification of ligninsulfonic acid to yield products similar to the higher polyphenols, and the polymeric aromatic sulfonic acids (e. g. the natural tannins and the syntans), would result in an effective tanning agent of the astringent type.

From the data of those who have studied the structural chemistry of the vegetable tannins [3], [4], [5] it is probable that not only phenolic, but carboxyl, ester, and alcoholic hydroxyl groups, as well as pyran oxygens, all function as polar portions of the molecule. However it is generally agreed that the phenolic hydroxyl group is responsible for the tanning reaction [6] and that the mechanism is essentially a hydrogen bonding of the phenolic groups to the peptide linkages of the collagen. This hypothesis has been supported experimentally by Tu and Lollar [7] in a comprehensive study of the tanning potential of a variety of phenolic compounds.

This work led Lipsitz, Lollar and O'Flaherty [8] to believe that proper chemical modification of lignin derivatives would result in an improved product which would overcome the objections to the unmodified lignin, and which would meet the requirements necessary for the production of commercial leather. They then carried out an extensive investigation, [9] in which a number of methods were used to increase the phenolic hydroxyl content of magnesium ligninsulfonate and of both softwood and hardwood alkali lignins. Amongst these methods were condensation with resorcinol and with phenol, which resulted in lignin derivatives with greatly improved tanning properties. In most cases, however, the products prepared in this way were insoluble in water, and were evaluated by solvent tannage, or were rendered water-soluble by treatment with sodium bisulfite. It was recognized that solvent tannage systems are impractical under present conditions in the tannery, and that the additional processing required to impart water solubility to the modified lignins would involve considerable additional cost which might render the process uneconomic.

The possibility of condensing ligninsulfonates with phenols to form water-soluble condensation products seemed to merit further investigation. All previous condensations of phenol with lignin appear to have been carried out under anhydrous conditions in the presence of an acid catalyst. F. E. Brauns [10], in his book entitled "The Chemistry of Lignin", has stated that "a purified calcium ligninsulfonate or free ligninsulfonic acid apparently does not condense with phenol in the presence of 1 per cent hydrogen chloride." However, a patent has been issued on the condensation of resorcinol with waste sulfite liquor in aqueous solution using hydrochloric acid as a catalyst. [11] The tanning properties of this condensate were evaluated by Highberger, Bump and O'Flaherty [12], and were found to be comparable to a vegetable tannage control, with the exception of a lower yield and a lower degree of tannage.

The results of preliminary work in our laboratories indicated that waste sulfite liquor could be condensed with various phenols under conditions which were much less rigorous than were thought to be necessary [13]. It has been discovered that the addition of an acid catalyst can be avoided by first removing the metallic ions from ligninsulfonates by ion exchange, and further, that anhydrous conditions are not necessary to effect a condensation between decationized ligninsulfonates and phenol. The conditions under which this reaction can be carried out have been carefully investigated. In this paper only a brief summary of this investigation, as well as some preliminary tanning results, will be presented.

Experimental

The raw material used in all our investigations was a commercial fermented waste sulfite liquor kindly supplied by the Ontario Paper Co., Ltd., Thorold, Ontario. No attempt was made to remove the residual sugars or other carbohydrate material, since the presence of small amounts of these substances during the tanning process was not considered detrimental.

The reaction between phenol and waste sulfite liquor was found to take place readily in aqueous solution at relatively low pH, namely 0.7 – 1.0. This low pH could be attained by the addition of a strong mineral acid, such as sulfuric acid, or by passing the waste sulfite liquor through a cation exchange resin operating on the hydrogen cycle. The latter method was considered to be preferable, since it obviated the need for removing sulfuric acid from the final tannin compound. Moreover, by this process, it is possible to adjust the pH of the phenol-ligninsulfonic acid condensation product to that required in the tannery, by the use of any desired alkali metal carbonate. If ammonia is used for this purpose, a completely ash-free tanning agent is obtained.

The ion-exchange resin used in these experiments was Amberlite IR - 120, manufactured by the Rohm and Haas Co., Philadelphia. Crude waste sulfite liquor, as supplied by the sulfite pulp mill, was passed through a large glass column containing this resin until the effluent showed a slight increase in pH, or tested qualitatively for calcium. The column was then regenerated with hydrochloric acid followed by water until a negative chloride test was obtained.

Effect of Degree of Decalcification of Waste Sulfite Liquor on its Reaction with Phenol

The pH of the ligninsulfonic acid is probably the most important variable in the reaction with phenol. Since pH is primarily a function of the degree to which the ligninsulfonic acid in waste sulfite liquor is neutralized by calcium, a series of experiments was carried out in which samples of decalcified waste sulfite liquor, to which various amounts of calcium were added, were heated with phenol under the same conditions. The results, shown in Table I, indicate that no reaction with phenol will take place when 43.6 per cent or more of the original calcium is present, and that the reaction is not inhibited by the presence of 10.9 per cent or less of the original calcium. In all subsequent experiments, however, a completely decalcified waste sulfite liquor was used.

TABLE I

Reaction of Phenol with Partially Decalcified Waste Sulfite Liquor

100 g. partially decalcified WSL solids (50 per cent solution w/v)
50 g. phenol
3 hours with stirring at 100°C.

CaO content (g/100 g. decalcified WSL solids)	% of CaO originally present in WSL	Degree of phenolation (g. phenol combined with 100 g. decalcified WSL solids)
14.9	100.0	0.
13.0	87.2	0.
6.5	43.6	0.8
3.25	21.8	8.8
1.62	10.9	11.7
0	0	11.5

The condensation of phenol with decalcified waste sulfite liquor in aqueous solution does not go to completion and it is necessary to extract the excess unreacted phenol with benzene or some other suitable solvent. From the weight of this recovered phenol it is possible to calculate the number of

grams of phenol which have condensed with 100 grams of decalcified waste sulfite liquor solids. This is arbitrarily defined as the Degree of Phenolation. This value may also be determined from the decrease in methoxyl content of the lignin resulting from the increase in its molecular weight by condensation with phenol. This latter method has been considered more reliable and has been used for calculating the results of this investigation. The yield of condensation product is approximately 98 per cent of the theoretical, since the only loss sustained is a small amount of water and sulfur dioxide split off during the reaction. The phenol recovered by solvent extraction may be re-used in subsequent condensations. A tentative flow sheet of the process is shown in Fig. I.

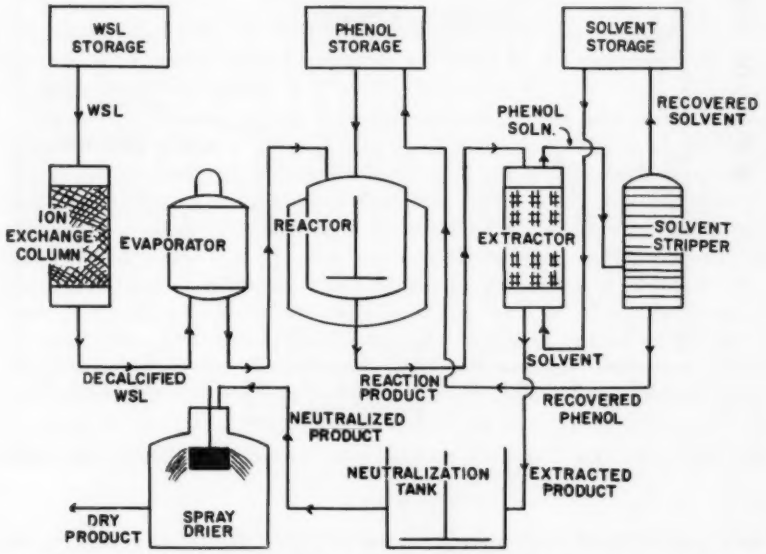


FIGURE 1.—Tentative Flow Sheet for Production of Tanning Agents from Waste Sulfite Liquor by Condensation with Phenol

The Preferred Conditions for Preparing the Phenol Condensation Product

Other factors which are known to affect the rate at which phenol condenses with the aqueous solutions of decalcified waste sulfite liquor are (a) time, (b) temperature, (c) concentration, and (d) the ratio of phenol to waste sulfite liquor solids. Some of the results which have been obtained during the investigation of these variables are summarized in Figure II.

The preferred reaction conditions for preparing the phenol derivatives are 3½ hours at 125°C., using a 30 per cent solution of decalcified waste sulfite

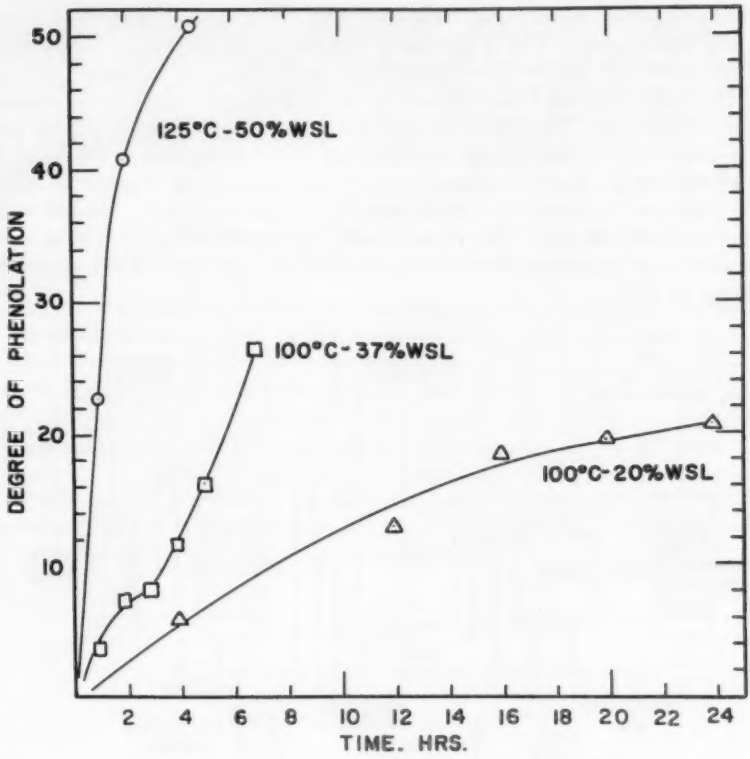


FIGURE II.—Effect of Time and Concentration on Reaction of Decalcified Waste Sulfite Liquor with Phenol.

liquor and an equal weight of phenol, based on the dry solids present in the decalcified waste sulfite liquor. By this procedure the degree of phenolation, after extraction of the excess phenol with benzene, is approximately 35, indicating that 35 grams of phenol have condensed with 100 grams of decalcified waste sulfite liquor solids.

It will be shown later that the tanning properties of the condensation product improve with increasing degree of phenolation. However, as might be also expected, the solubility of the condensation product decreases with increasing degree of phenolation, due presumably to the lower ratio of sulfonic acid groups. Our preferred conditions are designed to produce a completely soluble condensation product with a maximum degree of phenolation. Under more severe conditions, e. g. at higher temperatures or for longer

reaction periods, insoluble products are formed which cannot be used by the tannery without some additional solubilizing treatment.

Effect of Degree of Phenolation on the Tanning Properties of Phenol-Waste Sulfite Liquor Condensates

The effect of phenol condensation on the tanning properties of waste sulfite liquor has been demonstrated by comparing the properties of leather tanned with condensation products containing varying amounts of condensed phenol. The different condensation products were prepared by varying the conditions of the reaction, namely time, temperature, concentration of decalcified waste sulfite liquor, and per cent phenol in the reaction mixture, as described previously. The insoluble fraction which was formed in those experiments in which the Degree of Phenolation was in excess of 35, was removed by filtration prior to analysis and prior to the evaluation of these materials as tanning agents.

The tanning was carried out on small pieces of pickled cowhide grain split, approximately 4 inches by 6 inches, which were de-pickled with $NaHCO_3$–NaCl and treated with an acetate buffer at a pH of 5.0. Each sample was then agitated gently overnight in 100 ml. of a 2 per cent solution of the tannin, adjusted to a pH of 5.0 with sodium hydroxide. On the following day the tan liquor was adjusted to a pH of 4.0 with lactic acid and agitation continued for an additional 1½ hours. The hide was then transferred to 100 ml. of a fresh 3 per cent solution of tannin, adjusted to a pH of 3.5 with sodium hydroxide. After 3 hours contact, the hide was removed, washed with water at 40°C. for one hour and bleached with dilute sulfuric acid. The excess sulfuric acid was removed by washing and the samples staked out and allowed to dry slowly overnight. The properties of the resulting leathers are shown in Table II.

TABLE II

Effect of Phenol Content on Tanning Properties of Phenol-Waste Sulfite Liquor Condensates

	Phenol content (g. per 100 g. WSL solids)	Grain softness (decreasing)	Shrinkage temp. (°C)	Colour
1.	0 (decalcified WSL)	very hard	67.5	Light yellow
2.	9.8	5	74	Light gray-brown
3.	19.9	4	75	Medium gray-brown
4.	26.3	3	77	Medium gray-brown
5.	27.6	3	79	Dark gray-brown
6.	51.6	2	79	Medium gray-brown
7.	67.2	1	78	Dark gray-brown
8.	(Quebracho)	1	82	Red-brown

These results show that the tanning properties of waste sulfite liquor are improved by condensation with phenol, in direct proportion to the amount of combined phenol. In a further investigation, to be published later[14], it has been shown that no phenolic groups are destroyed during the condensation, and the resulting condensation product has a higher phenolic hydroxyl content than the original waste sulfite liquor. This evidence confirms the hypothesis that the tanning properties of lignin can be improved by increasing its phenolic hydroxyl content.

Effect of Insolubles on Tanning Properties of Phenol Waste Sulfite Liquor Condensates

From a commercial point of view, it is undesirable to filter off and reject an insoluble fraction, so that when ordinary phenol is used as the condensing agent it is impractical to go beyond a maximum degree of phenolation of approximately 35. It was of interest, however, to investigate the tanning properties of phenol condensates with somewhat higher degrees of condensation, both in the presence and in the absence of the insoluble fraction. Three such condensates have been prepared and their tanning properties evaluated by the method previously described. The results are shown in Table III.

TABLE III

Effect of Insolubles on Tanning Properties of Phenol-Waste Sulfite Liquor Condensates

Degree of phenolation (g. phenol per 100 g. WSL solids)		Percent insolubles (ALCA method)	Color	Softness (decreasing)	Shrinkage temp. °C*	Leather yield (g./100 g. original hide substance)
9	37.8	9.6	Gray brown	2	81.5	151
A (centrifuged)			Light brown	3	80.8	144
B	41.6	15.8	Gray brown	2	81.2	158
B (centrifuged)			Light brown	3	81.1	152
C	44.5	21.2	Gray brown	2	82.4	161
C (centrifuged)			Light brown	3	82.5	151
Waste sulfite liquor			Light yellow	4	70.2	129
Quebracho			Red brown	1	85.8	167

*The original hide used in these experiments had a shrinkage temperature of 63° C.

These results indicate a slight increase in shrinkage temperature with increased degree of phenolation. The highly colloidal insoluble fraction appears to be taken up by the hide, since its presence in the tannin solution increases the weight yield and imparts a softer but somewhat rougher grain to the leather. It apparently has no effect on shrinkage temperature.

Condensation of Decalcified Waste Sulfite Liquor with other Phenolic Compounds

A number of other commercially available phenolic compounds have been condensed with decalcified waste sulfite liquor under identical conditions, using in each case 0.68 mols of the phenol per 100 g. decalcified waste sulfite liquor solids and reacting for 4 hours at 125°C. The excess phenol in each case was recovered from the reaction mixture by extraction with a 50/50 mixture of ether and petroleum ether. The results are shown in Table IV.

TABLE IV

Reactivity of Various Phenolic Compounds with Decalcified Waste Sulfite Liquor

Reactants: 0.68 gram-mol. phenolic compound
294 ml. decalcified WSL containing
100 g. dry solids

Reaction Conditions: 4 hrs. at 125°C.

Phenolic compound	Degree of phenolation		Color of
	g/100 g. WSL solids	g.mols/100 g. WSL solids	aqueous solution
Salicylic acid (0.52 mols)	1.4	.010	Brown
Bis Phenol S (0.30 mols)	3.2	.013	Purple-red
B-Naphthol (0.52 mols)	12.7	.09	Purple-red
Vanillin	12.9	.09	Amber
Hydroquinone	11.4	.10	Brown
Catechol	16.2	.15	Brown
Phenol	21.3	.23	Brown
o-Cresol	26.2	.24	Brown
p-Cresol	26.3	.24	Brown
m-Cresol	31.7	.29	Brown
Resorcinol	41.8	.38	Red
Pyrogallol	57.0	.45	Red

Since the reaction conditions in each case were identical, the degree of phenolation was considered to be an approximate indication of the reactivity of the various phenols with decalcified waste sulfite liquor.

Tanning Properties of Various Phenolic Condensation Products of Waste Sulfite Liquor

A preliminary evaluation of the tanning properties of various polyhydric phenol derivatives of waste sulfite liquor has been carried out in much the

same manner as in the previous experiments. The properties of the resulting leathers are shown in Table V.

TABLE V

Tanning Properties of Polyhydric Phenol Condensates of Waste Sulfite Liquor

Tanning material	Degree of phenolation (g. per 100 g. WSL solids)	Color of leather	Shrinkage temp. °C*	Leather Yield (grams per 100 grams original hide substance)
A. Decationized waste sulfite liquor	——	Light brown, uneven	68	168
B. Phenol-decationized waste sulfite liquor condensate	40.8	Gray	76	174
C. 75 per cent B, 25 per cent quebracho	——	Light reddish brown	80	179
D. 50 per cent B, 50 per cent quebracho	——	Light reddish brown	83	215
E. Quebracho	——	Medium reddish brown	80	217
F. Resorcinol-decationized waste sulfite liquor condensate	32	Light reddish brown	88	189
G. Catechol-decationized waste sulfite liquor condensate	9.5	Medium bluish brown	77	189
H. Pyrogallol-decationized waste sulfite liquor condensate	32	Dark reddish brown	74	172

*The original hide used in these experiments had a shrinkage temperature of 63°C.

These results show that the tanning properties of the polyhydric phenol condensation products are superior to those of the phenol condensation product. This result was anticipated because of the higher ratio of phenolic hydroxyl groups introduced per unit weight of phenol and because of the presence of dihydric phenolic nuclei in the natural tannins.

Blends of these condensation products with quebracho effect a further improvement in tanning by increasing the hydrothermal stability and yield of the resulting leather. By determining the methoxyl content of these leathers it was possible to estimate the relative amounts of quebracho and condensation product taken up by the hide. It was found in every case that the condensation products were more slowly absorbed than quebracho so that the percentage of quebracho in the leather was slightly higher than it was in the original tannin solution.

Condensation of Waste Phenols with Waste Sulfite Liquor

The relatively high cost of the polyhydric phenols, in particular, catechol and resorcinol, would probably prohibit their use in the manufacture of tanning agents. The monohydric phenols are less satisfactory for this purpose, but are considerably less expensive. There are also available a number of crude phenol mixtures, which are recovered as by-products by other industries. Thus there appeared to be a possibility of producing a phenolic condensation product of waste sulfite liquor, with better tanning properties than the original waste sulfite liquor, at a substantially lower cost than the vegetable tannins.

This possibility has been investigated using a mixture of cresols recovered as a byproduct in the refining of petroleum. It is obtained by scrubbing the crude oil with caustic, essentially to remove sulfur compounds. By acidifying the crude caustic solution with carbon dioxide, the cresols separate out as an oily layer, leaving the mercaptans and other sulfur compounds in the aqueous solution. A simple distillation of this crude cresol mixture gave a light amber-coloured oil, free of low and high boiling residues.

This oil was condensed with decalcified waste sulfite liquor under a variety of conditions to produce a series of condensation products of varying degrees of phenolation. The reactivity of these waste cresols with decalcified waste sulfite liquor was quite similar to that of the pure ortho, meta and para cresols reported earlier. However, under the conditions required to produce a condensation product with the desired degree of phenolation, an insoluble fraction, amounting to approximately 25 per cent of the original materials, was obtained. This insoluble fraction was a soft tarry material which was filtered off and rejected. This was not considered to be a serious economic loss because both raw materials are waste products. An investigation of the tanning properties of the soluble portion has been carried out on a laboratory and pilot plant tannery scale[15].

Acknowledgments

The authors wish to express their appreciation to the Research Council of Ontario for financial assistance and for permission to publish this work. We are also indebted to Mr. W. R. Kenzie for carrying out the tanning tests and evaluating the experimental leathers.

Bibliography

1. Freudenberg, K., *Collegium*, **19**, 3 (1937).
2. Gustavson, K. H., *Tek. Tid., Uppl. C. Kemi.* **73**, 59 (1943); Ing. Vetenskaps. Akad. Handl. No. **177**, 82 pp. (1944).
3. Flinn, E. S., Nature of Chemical Components of Wood, TAPPI Monograph No. 6, 146 (1946).

4. Russel, A., *Chem. Rev.* **17,** 155 (1935).
5. White, T., *J. Soc. Leather Trades' Chemists,* **33,** 39 (1949).
6. Shuttleworth, S. G. and Cunningham, G. E., *J. Intern. Soc. Leather Trades' Chemists,* **32,** 183 (1948).
7. Tu, S. and Lollar, R. M., *J. Am. Leather Chemists Assoc.* **45,** 324 (1950).
8. Lipsitz, P., Lollar, R. M. and O'Flaherty, F., *J. Am. Leather Chemists Assoc.,* **44,** 399 (1949).
9. Lipsitz, P. and Lollar, R. M., *J. Am. Leather Chemists Assoc.,* **46,** 301 (1951).
10. Brauns, F. E., "The Chemistry of Lignin", p. 507 Academic Press (1951).
11. Schmidt, O., U. S. Patent 1,539,517 (May 26, 1925).
12. Highberger, J. H., Bump, A. H. and O'Flaherty, F., *J. Am. Leather Chemists Assoc.* **43,** 307 (1948).
13. Marshall, H. B., and Krizsan, M., U. S. Patent Application No. 299,278 (July 16, 1952).
14. Newcombe, A. G., Dignam, M., and Marshall, H. B., Paper presented at Canadian Pulp and Paper Association Annual Meeting, January 28, 1954.
15. Kenzie, W. R. and Wilson, A. M., Preparation and Tanning Properties of Phenolic Derivatives of Ligninsulfonic Acid. Part II. Application of the Cresol Derivatives to the Retanning of Chrome Leather. *J. Am. Leather Chemists' Assoc.* **50,** 96, (1955).

Received, Sept. 23, 1954.

The Preparation and Tanning Properties of Phenolic Derivatives of Ligninsulfonic Acid.

Part II. Application of the Cresol Derivative to the Retanning of Chrome Leather.

By W. R. Kenzie and Alison M. Wilson

Department of Biochemistry
Ontario Research Foundation
Toronto, Canada

In Part I of this paper, Marshall [1] described the preparation of a number of phenolic derivatives of ligninsulfonic acid. It was shown that these materials held considerable promise as tanning agents.

An estimate has been made of the production costs of these materials and it was found that the major cost item was the phenol required in the condensation. It was realized that a low-cost source of phenol would reduce the final cost of the tanning material appreciably.

Such a source was found in a petroleum by-product which consisted chiefly of cresols and was normally discarded as waste. The preparation of a condensation product from the purified cresols and ligninsulfonic acid was described in Part I.

This paper deals with the application of this condensation product in a light retannage of chrome leather.

Retanning Material

The preparation of the cresol derivative of ligninsulfonic acid has already been described.[1] The resulting material was in aqueous solution in the form of the free sulfonic acid. Part of it was reserved as such for use in the retanning procedure. The bulk was neutralized to pH 3 with sodium hydroxide and concentrated under vacuum to a solids content of 37.2 per cent. It was then ready for use.

The tannin content of the product was determined. The ALCA Method[2] was used, with the following exceptions: the shaking was carried out at 65 °C. in a constant-temperature shaking device known as the Launderometer, and the shaking period was extended to 30 minutes. The longer time and higher temperature were necessary because of the relatively lower reactivity of ligninsulfonic acid derivatives compared to vegetable tannins. The tannin purity determined in this way was 60 per cent on the total solids basis.

Baum[3] has shown that ligninsulfonic acid and other tanning materials when analyzed by the ALCA Method displace sulfate from the partially chrome tanned hide powder, and that this results in a high figure for non-tannins. The same phenomenon has since been noted in the case of the tannin analysis of the phenolic derivatives of ligninsulfonic acid, so that the figure for tannin purity is probably somewhat low.

Design of Experiment

A side of shaved chrome leather was obtained from a local tannery. The side was taken from regular production just prior to retannage. The water content of the leather was about 50 per cent.

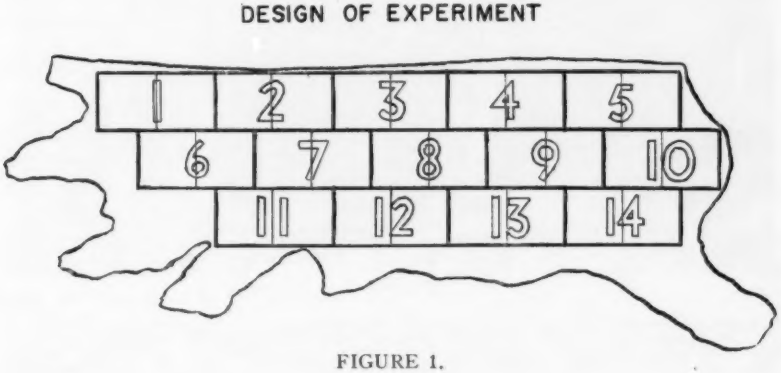


FIGURE 1.

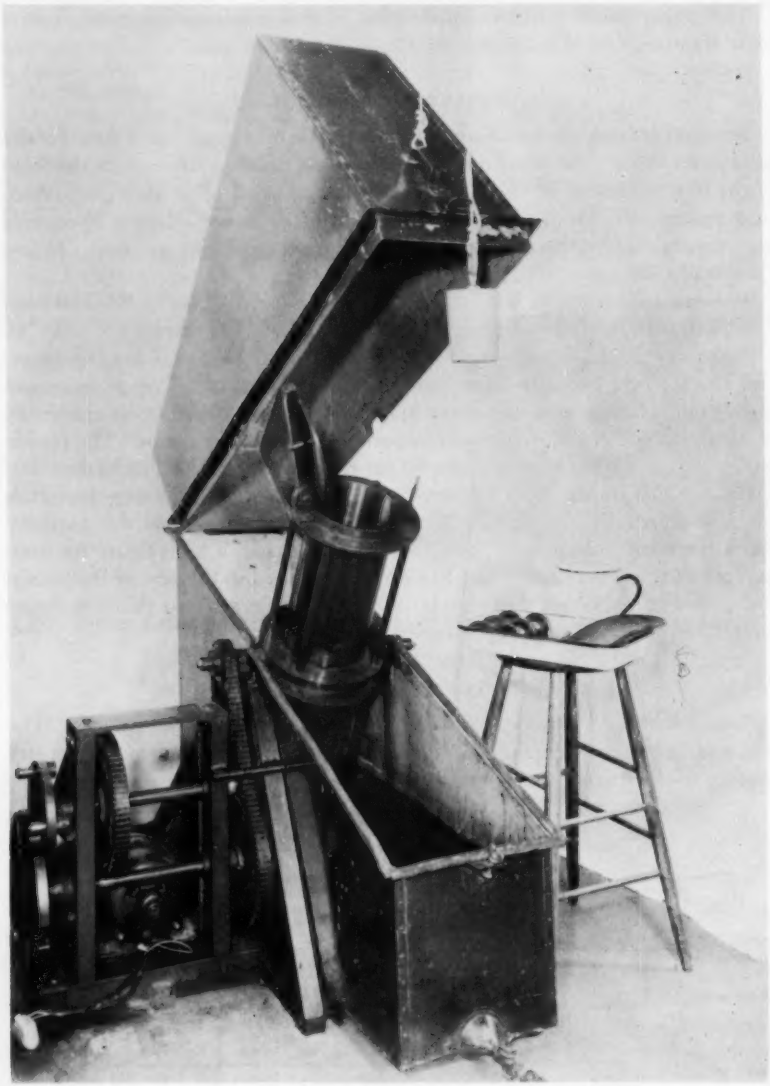


FIGURE 2.

The manner in which the hide pieces were cut from the side is shown in Fig. 1. Twenty-eight eight-inch squares were cut. The 28 squares were

divided into 14 pairs of adjacent squares. One square from each pair was retanned just as the side would have been retanned in the tannery, and the other square was retanned with the cresol derivative. The choice was made at random, by tossing a coin.

There were therefore 14 different local comparisons, covering practically the whole side.

Tanning Cylinder

For retanning the eight-inch squares of chrome leather, we used the apparatus shown in Figure 2. It consists of a stainless steel cylinder which rotates end-over-end in a tank of water the temperature of which is kept constant. The cylinder is driven by an arrangement of cams which stops it for a few seconds each time it reaches the vertical position. This allows the contents of the cylinder to fall through its full height of about 3 feet. Rubber covered steel balls are put in the cylinder along with the leather and liquor, in order to simulate the pounding action to which the leather is subjected in a tannery drum.

This tanning apparatus was copied from a previous design, and although the principle is not a novel one, it is described here to illustrate how the tannery process was simulated in the laboratory.

Retanning Procedure

A. *Normal Retannage*

The 14 pieces to be retanned by the normal tannery method were first weighed ("shaved weight") and measured with a thickness gauge.

The pieces were then washed for 20 minutes with occasional agitation in a bath of running water at 75°F. They were put into the tanning cylinder with 1 per cent of sodium bicarbonate and 20 per cent of water (quantities are expressed as percentages of the shaved weight). The cylinder was run for 25 minutes at 80°F. to neutralize the leather and then drained.

The leather after neutralizing was washed by running the cylinder for 20 minutes with 100 per cent of water at 80°F. The wash water was drained off.

Retanning was started with 100 per cent of water and 1.5 per cent of Leukanol solids (in 14.8 per cent solids solution at pH 1.4) at 80°F. The cylinder was run for 10 minutes, at the end of which time the pH of the tanning liquor was 4.0.

An amount of Lignosol solution of 17.5 per cent solids concentration was added corresponding to 1.5 per cent of Lignosol solids. The cylinder was run for 5 minutes at 80°F.

An amount of Chembark solution of 30.0 per cent tannin concentration was added which corresponded to 3.3 per cent of tannin. The cylinder was run for 20 minutes at 80°F.

Wattle extract of 11.6 per cent tan concentration was added in an amount corresponding to 3.6 per cent of tannin, and run for 30 minutes at 80°F. The spent liquor was then drained off and its pH was determined and found to be 4.0.

The leather was washed with 100 per cent of water at 80°F. for 10 minutes, drained, and allowed to stand for 2 hours.

The fatliquor was made up by warming 2 per cent of moellon degras with 2 per cent of sulfated cod oil and adding to 50 per cent of water at 130°F. The tanning cylinder and the leather were warmed up to 130°F. and the fatliquor was added. The leather was fatliquored for 25 minutes. At the end of this time the absorption of oil was complete.

The leather was drained overnight.

The fourteen pieces of leather were then pressed out by hand to remove the bulk of the water, and pasted to plate glass with wallpaper paste. The leather was dried slowly.

To remove the leather, damp towels were laid over the leather pieces for several hours to loosen the paste, and the leather was then peeled off the plate glass. The paste was immediately wiped off the leather with a damp towel. The leather was again allowed to dry. This procedure gave a leather free from the grain damage which tends to occur upon removal from the plate glass.

B. *Retannage with Cresol Derivative*

The preliminary treatment of the 14 pieces of chrome-tanned leather to be retanned with the cresol derivative was the same as described above for the normal retannage. That is, they were weighed, measured for thickness, washed, neutralized, washed again, and drained.

To the drained leather in the tanning cylinder was added 100 per cent of water at 80°F. and an amount of the cresol derivative at pH 1.4, in 15 per cent solids solution, equivalent to 1.0 per cent of tannin. (Quantities used are expressed as a percentage of the shaved weight). This corresponded to the Leukanol in the normal retannage. The cylinder was run for 10 minutes at 80°F. The pH of the liquor was then 3.7.

The first portion of cresol derivative at pH 3.0, in 22.3 per cent tannin solution, was then added. It consisted of 3 per cent of tannin. The cylinder was run for 20 minutes at 80°F.

The cylinder and contents were then warmed up to 100–105°F. over a 10 minute period. The second portion, consisting of 25 per cent of tannin, was added, and run for 20 minutes at 100–105°F.

The third portion, consisting of 2.0 per cent of tannin, was run with the leather for 20 minutes at 100–105°F. The leather was then drained. The spent liquor had a pH of 3.7.

The temperature of 100–105°F. was used to ensure proper uptake of the tanning material, which reacts more slowly than vegetable tannins.

The fatliquoring and drying were the same as for the normal retannage.

Appearance and Feel of Leathers

Both leathers were pale brown in color. The normal retannage was rather grayish, and the experimental retannage was more reddish and brighter.

The cross-section of all the normal pieces showed a blue streak, unpenetrated by the retanning material. Most of the experimental pieces also showed an unpenetrated layer, but to a lesser extent.

The feel of the two leathers was appreciably different. The grain surface of the experimental pieces was rougher than that of the normal pieces. The experimental pieces felt slightly fuller.

Chemical Analysis

The chemical analysis was performed according to the short method for retan leathers.[4] Composite samples of each leather were made up from the 14 pieces. The results of the analysis are shown in Table I. The table shows that the two leathers were similar in most respects and particularly that their degrees of retannage were nearly equal.

TABLE I

Chemical Analysis
(Moisture-Free Basis)

	Normal Retannage	Experimental Retannage
Hide Substance, Per cent	74.7	73.6
Total Ash, Per cent	3.83	3.81
Combined Acid Sulfate (as SO_4), Per cent	2.98	2.37
Chloroform Extract, Per cent	4.48	5.96
Combined Tannin (by difference)	14.0	14.3
	100.0	100.0
Degree of retannage (hide substance basis)	18.7	19.4
pH	3.16	3.26
Cr_2O_3, Per cent	2.61	2.47

Thickness Yield

The thickness yield of each piece of leather was determined by measuring the thickness before and after retannage. The thickness was measured in five places on each piece. The instrument used for measuring the thickness was a spring-loaded compressometer with a presser foot one inch in diameter.

In measuring the thickness, the presser foot was lowered onto the test area and a load of 135 grams was applied to the presser foot for one minute. The thickness reading in thousandths of an inch was taken.

The thickness yield was calculated as the final thickness of each piece as a percentage of its original thickness.

The mean thickness yields of the 28 pieces is shown in Table II. The difference between the Normal and Experimental pieces in each pair is shown in the last column.

TABLE II

Thickness Yield

	Thickness Yield, Per cent		
Pair No.	(1) Standard	(2) Experimental	Increase
1	100	97	—3
2	99	99	0
3	95	100	5
4	104	100	—4
5	101	100	—1
6	103	97	—6
7	104	102	—2
8	101	102	1
9	104	105	1
10	101	100	—1
11	107	94	—13
12	104	97	—7
13	104	110	6
14	106	101	—5
		Average Increase	—2 07
		Standard Deviation	4.91
		t	1.58

Table II would indicate that the experimental retannage gave a thickness yield which on the average was 2.07 per cent lower. However, the test for significance at a probability of 0.95 showed that the average difference of 2.07 per cent is not significant [5].

Tensile Strengths

The tensile strength of each piece was determined in duplicate. The results are shown in Table III. The last column shows the increase in tensile strength of the experimental over the normal retannage. The results showed that experimental retannage gave a leather which was significantly stronger than the normal leather.

TABLE III

Tensile Strength

	Tensile Strength, p. s. i. (Av.)		
Pair No.	(1) Standard	(2) Experimental	Increase
1	1660	1995	+ 335
2	1940	1870	— 70
3	2280	2740	+ 460
4	2600	2165	— 435
5	2505	1920	— 585
6	2710	2580	— 130
7	3110	3065	— 45
8	2445	2720	+ 275
9	2290	3385	+1095
10	1515	1910	+ 395
11	2180	2990	+ 810
12	2830	3260	+ 430
13	2270	3040	+ 770
14	2140	3680	+1540
		Average Increase	+ 346
		Standard Deviation	518
		t	2.2

Elongation

The elongation at break was determined simultaneously with the tensile strength and is shown in Table IV. The average difference was not significant.

TABLE IV

Elongation

	Elongation at Break, Per cent (Av.)		
Pair No.	Standard	Experimental	Increase
1	44	56	12
2	48	54	6
3	76	66	—10
4	—	—	—
5	66	53	—13
6	50	38	—12
7	54	42	—12
8	74	57	—17
9	62	56	— 6
10	54	62	8
11	29	38	9
12	10	42	32
13	—	—	—
14	44	26	—18
		Average Increase	—1.75
		Standard Deviation	15.13
		t	0.40

Stitch Tear Strength

The stitch tear strength of each piece was determined in duplicate by the former ALCA Method [2]. The results, along with the mean thickness measured at the test area, are shown in Table V. The experimental pieces were on the average stronger by about 6.3 pounds, but this difference was not significant.

TABLE V

Stitch Tear Strength

	Standard		Experimental		Increase,
Pair No.	Thickness, in. (av.)	Tear Load, pounds (av.)	Thickness, in. (av.)	Tear Load, pounds (av.)	pounds
1	.076	56	.077	111	+55
2	.084	113	.083	102	—11
3	.082	100	.083	100	0
4	.091	118	.089	110	— 8
5	.096	112	.095	88	—24
6	.072	86	.076	68	—18
7	.078	98	.082	112	+14
8	.088	82	.087	118	+36
9	.092	108	.090	120	+12
10	.080	77	.086	83	+ 6
11	.052	49	.077	78	+29
12	.068	111	.078	120	+ 9
13	.085	103	.076	83	—20
14	.084	92	.079	100	+ 8
				Average Increase	+6.3
				Standard Deviation	22.56
				t	1.04

Discussion

The results show that the experimental retannage with the cresol derivative gave a leather similar to a normal retannage. The chemical analyses were similar and there were no significant differences in thickness yield, elongation, or stitch tear strength. On the other hand, the tensile strength of the experimental retannage was significantly higher.

These findings recall the somewhat similar ones obtained by Zacharias [6] et. al., who found that the tear strengths and tensile strength of retan leather are improved when the vegetable retannage is replaced by a retannage with either Orotan or Exan.

We have also conducted tanning trials of the new material at two different tanneries. These trials confirmed our conclusion that the new tanning material produced a leather similar in most respects to a normally retanned leather.

Summary

The cresol derivative, prepared by condensing ligninsulfonic acid with a purified cresol waste, was evaluated as a retanning agent in comparison with a standard retannage giving a degree of retannage of about 20. The resulting leathers were similar in appearance and feel qualities and in degree of retannage. The tensile strength of the leather tanned with the cresol derivative was higher than that of the standard leather. The results, confirmed by tannery trials, showed the practicability of using the cresol derivative as a chrome retanning material.

Acknowledgments

The cooperation of A. R. Clarke & Co. Ltd., Toronto, and of the Robson Leather Co. Ltd., Oshawa, is gratefully acknowledged.

We are also indebted to Mr. W. C. Henry, Director of the Department, for his help and encouragement, and to Dr. D. B. Delury who cooperated on the statistical work.

References

1. Marshall, H. B., *J.A.L.C.A.*
2. A.L.C.A. Methods, 1946.
3. Baum, M., Camp, R. C., and Salvesen, J. R., *J.A.L.C.A.* **49**, 281 (1954).
4. Proposed Methods for analysis of chrome-vegetable retan leather *J.A.L.C.A.* **44**, 631 (1949).
5. Snedecor, G. W., Statistical Methods, Iowa State College Press, 1946.
6. Zacharias, W. B., Mann, C. W., Steiner, E. T. and Horkowitz, F. C., *J.A.L.C.A.* **48**, 460 (1953).

Received, Sept. 23, 1954.

Discussion

Martin Baum: I wish to congratulate Dr. Marshall, Mr. Kenzie and their associates on the work done in this paper. I think there is complete agreement in the statement that ligninsulfonate is not a replacement tannin, although there are similarities by reason of the phenolic hydroxyl groups.

It has been proposed that ligninsulfonate be improved as a tanning material by increasing its phenolic content. Thus it has been proposed that lignin be demethylated thereby forming one phenolic group per guaiacyl nucleus, or two phenolic groups per syringyl nucleus or by adding a phenolic resin or as in this case by forming a phenolic ligninsulfonate condensation product. This latter procedure was largely the basis of the so-called replacement tans that the Germans used during the last war.

One of the factors which affects the utility of such a product is, of course, the cost per tan unit as related to the cost per unit of vegetable tan. I would

therefore, like to ask Dr. Marshall how the cost per tannin basis compares between their product and the available vegetable tannins.

H. B. MARSHALL: We have attempted to estimate the cost of this product. It is difficult to estimate from the simple laboratory equipment we have used, what the final plant is going to cost. It is also difficult to estimate how rapidly you are going to be allowed to depreciate that plant. These costs are actually much greater than the cost of chemicals used in the process.

If the waste cresol derivative is the principal product manufactured, the raw materials would cost very little. These waste cresols are available for the cost of fuel oil. Waste sulfite liquor is a discarded product and the cost of regeneration would probably be in the neighborhood of three-quarters of a cent to a cent a pound.

We have also studied the possibility of regenerating with sulphur dioxide rather than hydrochloric acid. Sulphur dioxide is much less efficient and it is necessary to use a much higher molar ratio to regenerate the column. But it has the advantage that it is available at a sulfite pulp mill and the regenerated calcium bisulfite could be returned to the sulfite mill and re-used.

I cannot give an accurate answer to this question. We think it will be less than ten cents a pound, allowing for depreciation, profit and selling expenses, and all the other costs that are involved. But that is only an estimate.

BAUM: Now I would also like to ask: how close can the product be reproduced? In other words, is the condensation apt to progress further one time than another, and thereby give a larger fraction of insolubles?

MARSHALL: I think Dr. Baum is quite familiar with waste sulfite liquor and therefore knows how variable it is, and that is probably the reason that he asked this question.

I would say offhand that the amount of insoluble material may vary slightly from experiment to experiment. I do not think that this will be a more important factor than the amount of insoluble materials that are present in the natural tannins.

We anticipate that the process would be operated under such conditions that no insoluble fraction would be formed. This is true when dihydric phenols are used, or when phenol is used up to a degree of phenolation of about 40. I think there may be a slight difference from one product to another, but no more so than in any natural tannin product.

ABSTRACTS

Serial Experiments on Clarification of Waste Waters from Leather Factories in Worms. By Schlichting. *Das Leder* **5**, 214 (1954). Biological purification of waste waters from Worms tanneries was investigated. Other methods of purification, such as chemical flocculation, or filtration were impractical or too expensive. It was necessary to find out whether microorganisms could remove the chemicals (calcium and chromium salts and acids,-arsenic was absent) and convert the organic matter, (hide and leather waste) to fish food. Studies with fish in an aerated aquarium showed that fish could not survive in the tannery waste, even if it was diluted with 4 parts of city water per part of waste. Addition of 10% of city sewage (fecal water), however was sufficient to support microorganisms so that after 2 or 3 days aeration the water would support fish life for at least 14 days. Water from a brook, containing 50% sewage, was also effective in 10% concentration in purifying tannery waste water and the fish were found to devour the sludge. In a practical test the total waste water, 7000 cubic meters, from a tannery was treated at the factory exit with 700 cubic meters (10%) of the brook water daily. The waste flowed, at a rate of about 1 kilometer per hour through a 2 kilometer long canal to a settling pond. In 10 days the objectionable odor in the canal disappeared and algae and organisms were found at the pond edges. After 14 days, water from the pond was put in an aquarium and fish were able to survive in it. The test fish were goldfish, sheatfish, and bitterlings. I.D.C.

The Strength and Other Properties of Semi-Chrome Leather. A Study of the Effects of Some Factors Involved in the Semi-Chrome Processing of Split Hides. By M. F. Chambers, R. G. Mitton and E. F. Nattrass. *J. Soc. Leather Trades' Chemists*, **38**, 282 (1954). Due to complaints about semi-chrome leathers, it was decided to study the effect of modifications of the retanning process. The factors studied were: (a) the amount of vegetable tan retained after stripping; (b) the amount of chromium fixed in the leather; (c) the basicity of the chrome tannage and (d) the type of oil used in the fatliquors. For factor (a) stripping was done with 1 and 2 per cent sodium carbonate on the dry leather weight used. For factor (b) chromium was applied so as to yield 2-2½ per cent Cr_2O_3 on the basis of 66-75 per cent exhaustion; and also to yield half that amount. For factor (c) basicities of 32 and 40 per cent were used. For factor (d) a highly sulfated seal oil was used for one type of fatliquoring and a mixture of that oil with an unsulfated neatsfoot oil for another. Details of treatments and statistical analysis of results obtained are given. As a subsidiary investigation the effects of excessive temperatures in fatliquoring was studied. The effect on tensile strength, thickness, area, elongation at break, buckle-tear strength, compressibility modulus, water penetration pressure, shrink temperature, grease content and chromium content of grain and middle splits was determined. Only changes of chrome content gave any appreciable changes of strength; the higher amount of chrome reducing the strength by 11-13 per cent for the two leathers tested. The experiments described show that semi-chrome retannage results in increased strength as measured by the buckle-tear method, but not as measured by the tensile test. In both cases the higher chrome content gives the weaker leather. The leathers with the lower chrome content had lower shrinkage temperature, but what is more important from the practical standpoint, lower water penetration pressures. Apart from this observation there seems to be no reason why the chrome content of semi-chrome leather should be more than the minimum needed to give desired fullness and handle. The water repellency of the semi-chrome leather was greater in the leather of higher chrome content, in samples tanned in basic liquor, in those which were lightly stripped, and those fatliquored with oil containing only a small proportion of the sulfated component. The shrinkage temperature was

raised considerably in leathers that contained more chrome, was raised slightly by basic tannage and was raised when the vegetable tan was more thoroughly stripped. In the subsidiary experiment it was shown that wet semi-chrome leather shrinks little during prolonged heating at temperatures not much below its shrinkage temperature. It is therefore highly unlikely that any heat damage can be caused to semi-chrome leather at the temperatures commonly used in processing. R.H.T.

Heat Damage to Hides and Skins During Drying. By R. L. Sykes. *J. Soc. Leather Trades' Chemists*, **38**, 304 (1954). During recent years it has become apparent that the drying conditions encountered in tropical countries may result in hides reaching a temperature above the shrinking point of collagen. Hides so treated will not make strong leather. This work covers measurement of internal skin temperatures during drying under normal conditions in equatorial East Africa. Although it is only in ground drying that excessive temperatures are encountered, other drying conditions were also studied. The results obtained showed conclusively that temperatures higher than the shrinkage temperature of collagen are attained, when drying hides on the ground, and that leather made from such stock has little mechanical strength. The conditions conducing to this high temperature attainment are high atmospheric temperature, clear sky and absence of wind. R.H.T.

The Molecular Weight of Black Wattle Tannin. II. Substitution and Purification. By S. R. Evelyn. *J. Soc. Leather Trades' Chemists*, **38**, 309 (1954). Molecular weights determined from acetylated and diazomethane methylated tannins are compared. Commercial wattle extract was extracted with cold methanol until the extract contained 0.2 per cent total solids and gave a very faint coloration with ferric chloride, at which point it was concluded that all polyphenolic material extractable had been removed. The methanol solution was evaporated under reduced pressure and the dried residue used for the investigation. The dried extract was methylated and acetylated. Some of the extract was purified by removing sugars and gums. A modified Ray ebulliometric method was employed to determine the molecular weights of the methylated and acetylated tannin in benzene. The acetylated and diazomethane methylated materials gave different values for the molecular weights of the original tannins owing to the acetylation of nontan sugars and gums. Diazomethane substitution was found to give excellent and reproducible results. This reagent has the advantages of gentleness of action and elimination of nontan sugars and the bulk of the gums through non-reactivity. The calculated average molecular weights of tannins extracted by methanol from the commercial extract, using the diazomethane derivitive, were between 1200 and 1300. All the values for unfractioned tannins, obtained as above, lay between these limits. R.H.T.

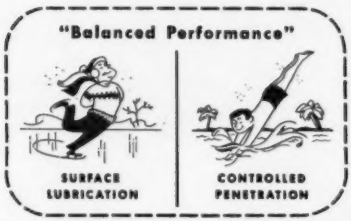
whether you tan for.....

or.....

NOPCOLENES GIVE YOU *Balanced Performance*

Equally important for both your "softy-type" leathers and the firmer types is the balanced performance you get to the highest degree only in famous Nopcolene® fatliquors. This balanced performance stems from the *dual action* of the two properties most necessary for finishing quality leathers—excellent *surface lubrication* plus *controlled penetration.*

This dual action of Nopcolenes give you a highly flexible control of all your leathers. It assures you not only of tight grain, good tensile strength, and stitch tear but it permits you to achieve the exact degree of temper, softness, hand, break, and stretch you wish to produce.



You'll find too that these Nopcolene fatliquors are readily soluble. Also, many of them are moisture-free; others contain not more than 6 to 7% moisture. This means real savings to you in freight, handling, and storage.

Write today for your FREE copy of the Nopcolene booklet, containing up-to-the-minute data and tannery-tested formulas for use with various leathers.

Nopco Chemical Co., 104 Bark St. Harrison, N. J.

NOPCO

PLANTS: Harrison, N. J. • Cedartown, Ga. • Richmond, Calif.

Sterozol

Reliable Germicide and Preservative

Sterozol is a non-coloring, non-interfering liquid which can be used in any wet operation:

- For inhibiting microbial action on hides and skins in process
- For inhibiting mold on stock and leather in process
- For preserving finishes

Sterozol's low relative toxicity, ease of handling, and economy have contributed in a large measure to its acceptance in the trade.

Sebacol

. . . for dependable unhairing

Sebacol produces clean, uniform, quality leather under varied beamhouse practices.

Biobate

. . . for effective baiting

Biobate provides controlled, effective enzymatic action during baiting for all types of leather.

WALLERSTEIN COMPANY, INC.

180 MADISON AVENUE • NEW YORK 16, N. Y.

Highest Quality

SODIUM SULPHIDE FLAKES

Our flakes dissolve into a PALE YELLOW SEDIMENT FREE solution, denoting an absence of IRON and other heavy metals. LEATHER MANUFACTURERS are especially pleased with our WATER THIN flakes because these flakes need not be pre-dissolved before using.

MANUFACTURED BY

BARIUM REDUCTION CORPORATION

SOUTH CHARLESTON, WEST VIRGINIA

BORNEO **CUTCH** EXTRACT

(MANGROVE BARK EXTRACT)

SAXE CUTCH CORPORATION

500 FIFTH AVENUE NEW YORK 36, N. Y.

Mardol TANNERY OILS

PURE TANNERY OILS AND FAT LIQUORS FOR ALL TYPES OF LEATHER

MARDEN-WILD CORPORATION

500 COLUMBIA STREET, SOMERVILLE, MASS.

MARDEN-WILD OF CANADA LTD., HALIFAX, N. S.

BETTER LEATHER IN LESS TIME...

... And with less trouble! Reports from tanners and finishers who use Sun's Leather-Processing Oils verify this. These oils make processing faster and easier because they mix easily, act fast, provide uniform fiber lubrication. Since they form no surface scum, tannage is even and thorough, leathers are stronger and better looking. For information, call your nearest Sun Office ... or write to Sun Oil Company, Philadelphia 3, Pa. *In Canada:* Sun Oil Company Ltd., Toronto and Montreal.

INDUSTRIAL PRODUCTS DEPARTMENT

SUN OIL COMPANY SUNOCO

PHILA. 3, PA. • SUN OIL COMPANY LTD., TORONTO & MONTREAL

Warner

BELL-MINE LIME

Year-round Uniformity
Dependable Source of Supply

WARNER COMPANY

Bellefonte Division, Bellefonte, Pa.

PITTSBURGH - - - - PHILADELPHIA - - - - NEW YORK

THE OHIO LEATHER CO.

Quality Calf Leather

LUXOR - BLACK JETTA
KAFFORITE - KOZY - JILL JETTA
EMBOSSED CALF - WHITE WASHETTE

TANNERY & GENERAL OFFICES: GIRARD, OHIO
BOSTON • NEW YORK • ST. LOUIS • CHICAGO

EISENDRATH FINE CALF LEATHERS

IN COLORS AND BLACK

B. D. Eisendrath Tanning Company

801 Merchandise Mart, Chicago, Ill. • Tannery at Racine, Wisconsin

92 South St., Boston, Mass., Day Gormley Leather Co. 29 W. 36th St., New York City, Eugene Williams

EST. 1908

MORITE BRAND

Sulphonated and Compounded

OILS

EST. 1908

WHITTEMORE-WRIGHT COMPANY, INC.
62 ALFORD ST. CHARLESTOWN DISTRICT BOSTON, MASS.

PRESTO

The Original Dry Color
for Splits and Suede
(also in paste form)

PRESTO COLOR COMPANY
WEST ALLIS 14, WIS.

Dry Colors ❖ ❖ Finishes

when you want

BORAX AND BORIC ACID HAVE LONG BEEN USED IN THE TANNING AND FINISHING OF GOOD LEATHER

borax or **boric acid**

think first of

SEND TODAY FOR FREE BOOKLET: "PROCESSING HEAVY LEATHER"

PACIFIC COAST BORAX CO.
DIVISION OF BORAX CONSOLIDATED, LIMITED
NEW YORK • LOS ANGELES • CLEVELAND • CHICAGO

Distributors located in principal cities throughout the U.S.A.

MANUFACTURERS OF FAMOUS "20 MULE TEAM" PACKAGE PRODUCTS

REILLY-WHITEMAN-WALTON CO.

OILS of CHARACTER

CONSHOHOCKEN, PA.

THE LEATHER MANUFACTURER

ESTABLISHED 1883

Exclusively a Tannery Paper

Devoted to Leather Technology, Tanning and Finishing of Leather, Tannery News and Markets.

Affords complete tannery coverage, concentrated among tanners, chemists and buyers of materials, raw stock and equipment.

Technical articles and newsworthy features invited for publication.

THE LEATHER MANUFACTURER

NEW YORK OFFICE
154 Nassau St.

BOSTON OFFICE
683 Atlantic Ave.

INSIDE TRACK TO BUSINESS!

Shoe and Leather REPORTER

TANNERY BUYER

THE TECHNICAL JOURNAL FOR SUPERINTENDENTS, CHEMISTS, TANNERS AND BUYERS

Why run around "Robin Hood's barn" when there's a quick direct route to customers?

The direct route to tanneries is by way of the TANNERY BUYER, a special monthly section of *Shoe and Leather Reporter*, made especially for and read by important executives, superintendents, chemists, and buyers.

Make your advertising dollars count. Use *Shoe and Leather Reporter's* TANNERY BUYER.

SHOE AND LEATHER REPORTER

Executive Offices: 207 ESSEX STREET, BOSTON 11, MASS.

Offices in: NEW YORK • CHICAGO • MILWAUKEE • CINCINNATI • ST. LOUIS • WASHINGTON • LONDON, ENG.

Salem Oil & Grease Co.

FAT LIQUORS

FEATURING

CONTROLLED PENETRATION

•

SALEM, MASSACHUSETTS

STANDARD HIDE POWDER

A material made to specifications and used internationally for the analysis of vegetable tanning materials

FRANK F. MARSHALL
RIDGWAY · PENNSYLVANIA

Garden State Tanning Inc.
Pine Grove, Pa.

Manufacturers of
Upholstery Leather

New York Office 330 Fifth Avenue

"The Extension of Knowledge is by the Investigation of Matter".

This space dedicated to
Tanners' Council Research Laboratory
by a Friend

KEPECO FINNALINE KEPOLAC
EMULLO KEEPA-SHINE FONDO
UNI-LAK
(Reg. U. S. Pat. Office)

KEPEC CHEMICAL CORPORATION
MILWAUKEE 1, WISCONSIN

finest products fastest service

TELEPHONE
BOulevard 8-2030

EST. 1924

TANNING EXTRACTS
SULFONATED OILS
STUFFING GREASES
LIGNOSULFONATES

ARTHUR C. TRASK CO.
4103 So. LaSalle St., Chicago 9
CABLE: *Actrask* TELETYPE: CG1478

2 to 1

That's the standing of LEATHER AND SHOES in the tanning industry

The latest circulation statement shows that LEATHER AND SHOES has 141% more paid and audited circulation among tanners (audited by the Audit Bureau of Circulations). That's more than double the number of paid subscribers of any other magazine.

But *readership* is even more important. A recent study revealed that at least 3500 top level executives in the tanning industry are reading LEATHER AND SHOES.

Consider the facts: LEATHER AND SHOES—
. . . does the outstanding job in editorial service.
. . . has twice the paid circulation and considerably more readership.
. . . carries more than double in advertising volume.
. . . does *not* sell advertising on its front cover.
. . . is the industry's most dynamic business paper.

An investment in a subscription to LEATHER AND SHOES will pay dividends in knowledge—an investment in advertising in LEATHER AND SHOES will pay dividends in success. If you want more facts, write us today.

L&S

LEATHER AND SHOES
300 W. ADAMS STREET
CHICAGO 6, ILLINOIS

Finishes
for all types of
Leather

FINE LEATHER FINISHES NLF

NEWARK
LEATHER FINISH CO.

8 WILHELM ST. HARRISON, N. J.
Telephone: Humboldt 5-3470

HOWES LEATHER CO. INC.

SOLE LEATHER

•

Tanners Cut Sole Division

•

CUT SOLES

BOSTON, MASS.
ST. LOUIS, MO. CHICAGO, ILL.

BONA ALLEN, INC.
Buford, Georgia

TANNERS SINCE 1873

•

Finest English Rein
and Strap Leather

Latigotan Harness Leather

Manufacturers of genuine English type and full rigged hand tooled roping saddles.

A TRIUMPH IN TANNING RESEARCH!

Years of laboratory and tannery
experimentation are now climaxed by a

NEW, PROVEN
TANNING MATERIAL

that provides surprisingly superior results

•

AVAILABLE SOON IN
UNLIMITED QUANTITIES

"FORESTAN"

(Reg. Pending)

•

WATCH FOR THIS INNOVATION THAT IS
CERTAIN TO CHANGE & IMPROVE PRESENT METHODS

LEATHER FOR HEALTH AND DISTINCTION

LEATHER WILL BE WITH US ALWAYS

LEATHER and TANNING MATERIALS

CONSULTING • TESTING • RESEARCH • DEVELOPMENT
for the
TANNING AND ALLIED INDUSTRIES

Specialists: Sampling and Testing of Tanning Materials

UNITED STATES TESTING COMPANY

INCORPORATED
1950 Park Avenue, Hoboken, N. J.

THE TANNERS' COUNCIL RESEARCH LABORATORY

at

THE UNIVERSITY OF CINCINNATI

is

THE DEPARTMENT OF BASIC SCIENCE

in

THE GRADUATE SCHOOL OF ARTS AND SCIENCE

The purpose of the laboratory is to conduct scientific research in the fields of Science concerned with Tanning and Leather.

To train Chemists in the technique of research and prepare them for Industry.

This Laboratory serves as the Official Technical Headquarters for the Tanning Industry of the United States.

Your inquiries will be gladly answered.

Address DR. FRED O'FLAHERTY, Director
Tanners' Council Laboratory
University of Cincinnati
Cincinnati 21, Ohio.

VELVETEEN BLACK

A BRIGHT, DEEP BLUE-BLACK NON-INFLAMMABLE FINISH, FOR PLATING OR GLAZING.

USE ON FULL GRAIN OR CORRECTED LEATHERS.

EVEN SPREADING - EXCELLENT COVERAGE
GOOD TIGHTNESS TO WET RUBBING

SAMPLE ON REQUEST

APEX
MARK of QUALITY
Established 1900
Apex Chemical Co., Inc.
225 West 34th St., New York 1, N. Y.

Manufacturers of a complete line of specialties for the tanning trade

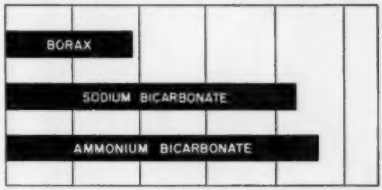
UNION TANNERS SUGAR LIQUID, CHIPPED, BILLETS
UNIFORM CLEAR NON-FOAMING UNIFORM CLEAR
UNION TANNERS SUGAR LIQUID, CHIPPED, BILLETS
NO NG
UN ETS
UN AR
UN ETS
NON-FOAMING UNIFORM CLEAR NON-FOAMING
UNION TANNERS SUGAR LIQUID, CHIPPED, BILLETS
UNIFORM CLEAR NON-FOAMING UNIFORM CLEAR

UNION STARCH & REFINING CO.

Established 1903
General Offices. COLUMBUS, INDIANA

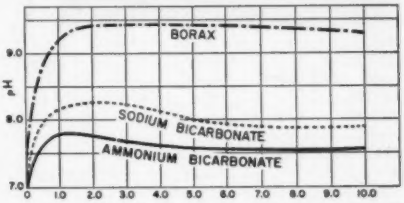
Here's why SOLVAY Ammonium Bicarbonate does a better job of neutralizing

1. Higher Neutralizing Power



Pounds of hydrochloric acid neutralized by 1 lb. of alkali

2. Lower pH



Comparative pH of solutions at various concentrations

. . . and gives you these 6 OUTSTANDING ADVANTAGES:

1. Upgrades leathers!
2. Improves grain!
3. More uniform dyeing!
4. More efficient neutralizing!
5. Low pH safeguards against over-neutralizing!
6. Faster penetration!

Superior leathers are obtained with SOLVAY Ammonium Bicarbonate—because it penetrates the leather uniformly throughout the thickness of the hide—the inner part as well as the surface. SOLVAY Ammonium Bicarbonate has a *high neutralizing* value (greater than borax or sodium bicarbonate) with a *low* pH. A 1% solution has a pH of only 7.8!

Send for Test Samples of SOLVAY Ammonium Bicarbonate and see how it gives you *better looking leathers—economically* and *efficiently*. Write or phone the SOLVAY office nearest your plant.

SOLVAY PROCESS DIVISION

Allied Chemical

ALLIED CHEMICAL & DYE CORPORATION

61 Broadway, New York 6, N. Y.

BRANCH SALES OFFICES:

Boston • Charlotte • Chicago • Cincinnati • Cleveland • Detroit • Houston
New Orleans • New York • Philadelphia • Pittsburgh • St. Louis • Syracuse

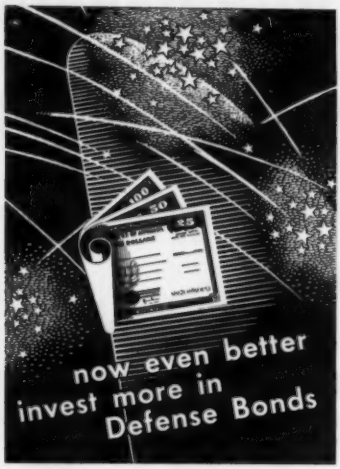
SOLVAY

Other Solvay Products for Tanners

- **CLEANSING SODA XX**
- **SNOWFLAKE* CRYSTALS**

*REG. U. S. PAT. OFF.

Soda Ash • Snowflake® Crystals
Potassium Carbonate
Calcium Chloride
Sodium Bicarbonate
Ammonium Bicarbonate
Cleaning Compounds
Caustic Potash • Sodium Nitrite
Ammonium Chloride • Chlorine
Caustic Soda • Chloroform
Monochlorobenzene
Para-dichlorobenzene
Ortho-dichlorobenzene
Methylene Chloride
Methyl Chloride
Carbon Tetrachloride



RESEARCH

has Two functions

To produce a better Product and
to do it More Economically.

THE TANNERS' COUNCIL
RESEARCH LABORATORY
UNIVERSITY OF CINCINNATI

RESEARCH
PAYS DIVIDENDS

when Properly Applied.

THE TANNER'S COUNCIL
RESEARCH LABORATORY
University of Cincinnati

INDEX TO ADVERTISERS

AMERICAN CYANAMID COMPANY, Dyestuff Department XIX
AMERICAN CYANAMID COMPANY, Leather Chemicals Department XI
AMERICAN EXTRACT CO. ..... Outside Back Cover
APEX CHEMICAL CO., INC. XXXVI
ARKANSAS COMPANY, INC. V
ARTHUR C. TRASK CO. XXXI
ARTHUR THOMAS CO. XXII
ATLAS REFINERY XIII
BARIUM REDUCTION CORPORATION XXV
BARKEY IMPORTING CO., INC. XVIII
BONA ALLEN, INC. XXXIII
BUCKMAN LABORATORIES, INC. XII
CHEMTAN COMPANY XXI
EISENDRATH TANNING CO. XXVII
EUROPEAN CHESTNUT MFG'S ASSO. XVI
FORESTAN XXXIV
FRANK F. MARSHALL XXXI
GARDEN STATE TANNING INC. XXXI
GEIGY COMPANY, INC. IX
GENERAL DYESTUFF COMPANY ..... Insert
HOOKER ELECTROCHEMICAL CO. XVII
HOWES LEATHER CO., INC. XXXIII
INTERNATIONAL PRODUCTS CORP. X
KEPEC CHEMICAL CORPORATION XXXI
LEATHER AND SHOES XXXII
LEATHER MANUFACTURER, THE XXIX
L. H. LINCOLN & SON, INC. VIII
MARDEN WILD CORPORATION XXVI
MEAD CORPORATION, THE VI
NEWARK LEATHER FINISH CO. XXXIII
NOPCO CHEMICAL CO. XXIII
OHIO LEATHER CO., THE XXVII
OLSON SALES AGENCY, THE ..... Inside Front Cover
PACIFIC COAST BORAX CO. XXVIII
PRESTO COLOR CO. XXVIII
REILLY-WHITEMAN-WALTON CO. XXIX
RIVER PLATE CORPORATION, THE XIV
ROBESON PROCESS CO. II
ROHM & HAAS IV
SALEM OIL & GREASE CO. XXX
SAXE CUTCH CORPORATION XXVI
SHOE & LEATHER REPORTER XXX
SOCONY-VACUUM OIL CO. I
SOLVAY PROCESS DIVISION, ALLIED CHEMICAL & DYE CORP. XXXVII
SOUTH AFRICAN WATTLE EXTRACT MFRS. ASSO. XV
SUN OIL COMPANY XXVI
TANEXCO, INC. ..... XL—Inside Back Cover
TANNERS' COUNCIL RESEARCH LABORATORY ..... XXXI—XXXV—XXXVIII
TEAS EXTRACT CO. III
UNION STARCH & REFINING CO. XXXVI
UNITED STATES TESTING COMPANY XXXV
WALLERSTEIN COMPANY, INC. XXIV
WARNER CO. XXVII
WHITTEMORE-WRIGHT CO. XXVIII
WOLF, JACQUES & CO. VII
YOUNG CO., J. S. XX

ITALIAN

CHESTNUT EXTRACT

Solid — Powder — Spray Dried

also

MELLOWED CHESTNUT

Highly Soluble — Weight Giving — Good Color

MADE FROM LIVE WOOD

TYPICAL A.L.C.A. ANALYSIS

	Solid	Mellowed Powder	Spray Dried
TANNIN	61.72	65.95	73.5
NON-TANNIN	21.65	26.67	19.1
INSOLUBLES	.65	.67	.7
WATER	15.98	6.71	6.7

STAINLESS SUMAC CRYSTALS

CIPEC

HIGHEST QUALITY—MADE UNDER THE SUPERVISION OF THE WORLD'S LEADING EXTRACT CHEMISTS

SOLE AGENTS

TANEXCO, INC.

549 W. Washington Blvd. Chicago, Illinois

MYRTAN

A TANNING EXTRACT

made from the wood of an Australian species of the Eucalyptus family. It contains both catechol and pyrogallol tannin, the latter predominating.

TYPICAL A.L.C.A. ANALYSIS

	Ordinary	Clarified
TANNIN	61.55	64.34
NON-TANNIN	16.03	17.14
INSOLUBLES	1.70	0.72
WATER	20.72	17.80

Also Available as Liquid with 30% Tannin

As a retanning agent for chrome tanned leather, Myrtan possesses many advantages, such as smooth and strong grain, good color and break, as well as a round feel.

Blended into sole leather tannages, it has given better yields and improved color.

For further information address.

TANEXCO, INC.

549 WEST WASHINGTON BLVD., CHICAGO 6, ILLINOIS

SOLE AGENTS
U. S. A.

DERMABATE COMPOUNDS LIQUID EXTRACTS

HEMLOCK
OAK
MANGROVE
WATTLE
STAINLESS SUMAC
ORDINARY SUMAC
QUEBRACHO
SPECIAL DIPPING EXTRACTS
RAPID TAN "G"

★

AMERICAN EXTRACT CO.

Manufacturers of the Largest
Variety of Vegetable Tanning Extracts
Established 1887
PORT ALLEGANY, PA.

CANADIAN REPRESENTATIVES:
McArthur Chemical Co., Ltd., 20 St. Paul St., West, Montreal: 73 King St., West Toronto

ENGLISH REPRESENTATIVES:
Roy Wilson, Dickson, Ltd., 7-8 Railway Approach, London, S. E. 1